

SOUTHERN CALIFORNIA PARTICLE SUPERSITE

Progress Report for Period February 1, 2001 - May 1, 2001

United States Environmental Protection Agency

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1. Introduction

The overall objective of the Southern California Particle Supersite is to conduct research and monitoring that contributes to a better understanding of the measurement, sources, size distribution, chemical composition and physical state, spatial and temporal variability, and health effects of suspended particulate matter (PM) in the Los Angeles Basin (LAB). The specific research objectives are:

1. To characterize PM, its constituents and precursors, to better understand sources and transport which may affect human exposure and to support development of State Implementation Plans (SIPs).
2. To obtain atmospheric measurements for the support of health studies that are designed to address causal factors, etiologic pathways and mechanisms of PM related morbidity and mortality with particular emphasis on PM source-receptor-exposure-effects pathways.
3. To conduct methods testing that will enable comparisons and evaluation of different technologies for characterizing PM, including evaluation of new instrumentation, sampling methods and federal reference methods.

This report addresses the period from February 1, 2001 through May 1, 2001

2. Particulate Sampling at Downey and Riverside, CA

During the first half of February 2001, we have continued our PM sampling at Rancho Los Amigos (south-central Los Angeles), in conjunction with ongoing human inhalation exposure studies to concentrated PM, as well as studies in which we use our coarse, fine and ultrafine concentrators to collect size-fractionated PM for *in vitro* characterization of PM toxicity. These studies are part of our PM Center Toxicology core investigations as well as our collaborative efforts with Dr. Robert Devlin (US EPA). The Particle Instrumentation Unit (PIU) was deployed to our second Supersite sampling site, in Riverside CA, during the 3rd week of February 2001. Sampling at Riverside started during the last week of February. Contrary to Downey, which is considered a “source” site, directly impacted by vehicular emissions by nearby freeways, Riverside is a USC Children’s Health Study site, which the urban aerosol reaches after “maturing” or “aging” for several hours in the atmosphere.

During the period covered by this progress report, we have completed all of the PM speciation analysis for data collected in Downey. In addition, we have completed the analyses of our continuously generated PM data in Riverside through the end of March, 2001. These data will be presented in the following paragraphs.

2a. Time-integrated data

Our current sampling scheme involves the use of three MOUDI for 24-hour averages, size-fractionated measurements of ambient and concentrated PM mass and chemical composition. Sampling is conducted once a week, on a Tuesday, Wednesday or Thursday, in order to coincide with one of the sampling days of the AQMD speciation network (which takes place every 3rd day).

In each run, consistent with our original Supersite proposal, we have used three collocated Micro-Orifice Uniform Deposit Impactors (MOUDI) to group PM into the following size ranges:

- <0.1 μm (ultrafine particles)
- 0.1- 0.35 μm (accumulation mode, “condensation” sub-mode)
- 0.35 -1.0 μm (accumulation mode, “droplet” sub-mode)
- 1.0-2.5 μm (“intermediate” mode)
- 2.5-10 μm (coarse particles)

In addition to mass concentration, the following chemical components have been analyzed within these size groups:

- a. inorganic ions (i.e., sulfate, nitrate, ammonium)
- b.** trace elements and metals
- c. elemental and organic carbon (EC/OC) content
- d.** concentrations of polycyclic aromatic hydrocarbons (PAH)

Ambient data are averaged over 24 hours, whereas data corresponding to concentrated PM are only averaged over two hours, as this is the typical duration of the human exposure experiments, conducted simultaneously with PM sampling.

In addition to the MOUDI, we employ two dichotomous samplers:

- a. Partisol-Plus sampler (Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co. Inc., Albany, NY; and
- b. USC Dichotomous Sampler, operating at 50 LPM, which will be described in greater detail by Misra et al. (2001)

These two samplers are used to provide data on mass and chemical compositions of coarse (2.5 – 10 μm) and fine (0-2.5 μm) particles in the following time intervals: 6 am –10 am; 10 am – 3 pm; 3 pm- 8 pm; 8 pm – 6 am. These experiments are also conducted approximately once every 3rd day and concurrently to the MOUDI sampling days. In each of the coarse and fine particle channels of the Partisol sampler we place quartz filters for PM collections, whereas Teflon filters

are placed in the coarse and fine PM channels of the USC Dichotomous sampler. At the end of each test, a 0.2 cm² portion of the Partisol quartz filters are removed and sent for elemental and organic carbon (EC/OC) analysis, whereas the remaining filter was extracted with milli-Q water to determine the inorganic ion content of coarse and fine PM. The USC Dichotomous Sampler filters were first weighed to determine the mass concentrations and then analyzed by means of XRF to determine the trace element and metal content of coarse and fine PM.

Sampling has been completed for a total of 16 weeks covering the period from October 3, 2000 to February 2001 and all samples have been analyzed. Figures 1 to 5 show the average chemical compositions of the five PM₁₀ submodes. Over 80% by mass of ultrafine PM are carbonaceous, with the average elemental and organic carbon contents being 18% and 64%, respectively. Organic carbon (69%) and nitrate (14%) are the two most prominent constituents of the condensation mode (0.1-0.32 µm). The mass fraction of nitrate increases as PM size increases to the droplet and intermediate modes. Organic carbon is still an important species of the droplet mode, accounting on the average for 47% of the PM mass in that size range, whereas the nitrate content is about double (i.e., 28%) that found in the condensation mode. The intermediate mode consists primarily of trace elements and metals (38% by mass), organic carbon (24%) and nitrate (14%). Finally coarse PM consist mainly of trace elements and metals (about 60%), whereas organic carbon accounts for about 24% of coarse PM by mass. Sulfate contributes less than 4-6% to the total PM₁₀ mass in south-central Los Angeles. Figures 1-5 also indicate that overall excellent agreement was obtained between the sum of the chemical concentrations of each species for each mode and the gravimetrically determined mass concentration. In general, the chemical speciation data could explain between 85-100% of the total measured mass in each PM₁₀ sub-mode.

Figure 6 shows a plot of the most abundant metals in the coarse and fine PM modes, plotted as function of their total mass fraction. Al, Si, Fe, Ca, K, Cl, S and Ti are the most abundant metals in the coarse and fine modes by mass, with the mass fractions of the coarse mode being generally higher than those of the fine PM. A more detailed plot of the of the average partition by mass in

the five PM size modes of the 17 most predominant metals and elements at Rancho Los Amigos is shown in Figure 7. The data plotted in Figure 7 reveal that Al, Si, Fe, Na, Ca, K, Ti and Mg are almost exclusively partitioned in the super micrometer size range, with more than 50 to 60% by mass found in the coarse mode. About 30-50% of the mass concentrations of Si, Ca, Ti, Fe, Mg and Cu are found in the intermediate (1-2.5 μm) mode. Combustion-generated metals and elements, such as Zn, Cu, Mn, Pb, Cr, Sn, V and Ni are associated largely with PM_{2.5}, with mass fractions varying from 0.75 to 0.93. Ultrafine and condensation mode particles account for more than 40% of Pb, Cr, Sn, V and Ni.

Figures 8 and 9 show average temporal trends in the concentrations of the most predominant metals in the coarse and fine PM modes, respectively. The diurnal trends in the concentrations of each metal are quite similar; in the coarse PM, the concentrations become higher in the afternoon (between 2-6 pm) and drop sharply at night (Figure 8). By contrast, the metal concentrations for fine PM peak in the early morning period (6-10 am) and decrease during the day. These two observations can be further explained by examining the relationship between wind speed at Downey and time of the day, which is plotted in Figure 10. In general, the average wind speed reaches a maximum in the afternoon, between 2 and 6 pm and decreases later in the evening and during the early morning hours. Coarse PM that are primarily produced by wind resuspension are thus higher during the time at which the wind speed reaches a maximum. Fine PM metals, which, at least at Downey, mostly originate from vehicular emissions, become maximum during the early morning period in which traffic peaks, the atmospheric mixing layer is at a minimum and the wind speed (which would dilute the emissions) is also at a minimum. The fine PM-bound metals reach a minimum during the afternoon period, because of the increase in mixing layer and wind speed, both of which tend to disperse the vehicular emissions of the nearby freeways, and increase again during the nighttime, because of the decrease in wind speed (Figure 10) and decrease in atmospheric mixing layer.

About 25.4 (\pm 5.8) % of coarse particles is associated with organic carbon. Figure 11 shows the mass fractions of selected PAH in coarse particles, expressed in ng of PAH per mg of

particulate mass. The total average PAH contribution is about 31.3 (\pm 8.9) ng of PAH per mg of PM. Acenaphthene, phenanthrene, pyrene and benzo(ghi)perylene are the most predominant PAH in coarse PM, with mass fractions varying from 3 to 7 ng per mg PM. Fine PM are substantially more enriched in PAH (Figure 11) with their average fraction being 138 (\pm 38) ng per mg of fine PM mass. This is about four times higher than the contribution of PAHs to the coarse PM. Phenanthrene, pyrene, fluoranthene, benzo(a)pyrene and benzo(ghi)perylene are the most predominant PAH in fine PM, with mass fractions varying from 8 to about 30 ng per mg PM.

2b. Continuous PM Size Distributions

Near-continuous (i.e., 15-min averaged) size distributions for 0.01 – 10 μ m particles were generated by means of the SMPS (0.01- 0.8 μ m) and APS (0.5 – 10 μ m) monitors. The size distributions generated by the two instruments were matched at 0.5 μ m using a standard particle with a density of 1.6 g/ml. We have refined the representation of our continuous PM size distributions by making use of contour plots of the number and/or volume-based concentration as a function of particle size and time of the day. Indicative size distributions as function of time of day for either Downey or Riverside are shown in Figures 12 to 19. In general, our field experiments have shown that the following parameters play a very significant role in affecting the PM size distribution characteristics:

- a. Site location (source vs receptor)
- b. Wind speed and direction
- c. Time of the day (affecting temperature, mixing height and dispersion of urban plume)

Stagnation periods (i.e., wind speed less than 2 mph) favor higher concentrations of ultrafine and fine PM (as evident by the data plotted in Figures 12 and 13) and lead to lower coarse PM concentrations. Windy conditions, such as those observed on February 27, 2001 at Riverside (with wind speeds through the day exceeding 7 mph) tend to dilute the fine PM concentrations

and lead to increased coarse PM concentrations. The minimum in the fine PM concentration observed during the middle of that day can be explained by the increase in wind speed to over 10 mph and the wind direction, which unlike a typical day, which was directly from the east to southeast, thus in the opposite direction of Los Angeles or the ammonia sources of the nearby Chino area farms. Similarly, on April 15, 2001, the wind direction changed from the typical west-to-northwest to directly northeast (i.e., from the direction of the California deserts). This affected dramatically the coarse PM concentrations, as shown in Figure 14, leading to very high concentrations through the day in the super-micrometer range. A similar example is shown in Figure 15 (February 22, 2001 in Riverside), in which the change in the wind direction from southwest to east led to increased coarse particle concentrations.

Figures 16 and 17 show a more “typical” temporal profile of volume-based PM₁₀ size distributions in Downey and Riverside, respectively. At Downey, the highest PM concentrations in most of the size distributions were observed in the 6 am – 10 am period, followed by the nighttime (8 pm – 6 am) period. The high PM concentrations in the 6am – 10 am period are obviously due to the contributions of morning traffic. The high PM concentrations at night are due to the 24-hour heavy diesel truck traffic in the nearby 710 (Long Beach) Freeway, combined with the low mixing layer of the atmosphere at that time. The Rancho Los Amigos Supersite monitoring site is located approximately 1.6 km east of freeway 710, thus directly downwind of the freeway.

The peak in the mass concentrations of the accumulation mode in Riverside during the late afternoon hours can be attributed to some degree to photochemical reactions, which would peak during the afternoon. These reactions are expected to be more pronounced during the warmer months of the year in Los Angeles (i.e. June to November), but there are still significant sources of PM in Los Angeles even during the cooler months (Luhrman et al., 1997). In addition to the photochemical activity, the arrival of the urban aerosol, originally emitted by vehicular sources around downtown Los Angeles, may also be responsible for the increased fine PM concentrations in the afternoon. This hypothesis can be further supported by examining the relationship

between wind speed and direction and time of the day in Riverside, which is illustrated in Figures 18 and 19, respectively. The data plotted in these figures indicate a remarkably consistent pattern, despite some scatter due to differing meteorological conditions. The wind speed increases from the 2-3 mph range to the 8-10 mph range during the daytime, starting at about 9 am. The wind direction also changes from southeast (during the nighttime) to northwest during then daytime, and changes abruptly in speed and directions some time during the early evening hours (after about 7 pm). This implies that during the daytime, the wind is blowing for the direction of Los Angeles. Considering that downtown Los Angeles is about 50 to 60 miles east of or Riverside site, fine aerosols emitted mostly during the early morning traffic hours should arrive in Riverside by 5 to 6 pm, which is the period during which the highest concentrations are observed. Further details on the chemical composition of PM in Riverside, which will be presented in our next progress report, will help identify the degree and prevalence of each of these two PM formation processes.

2c. Studies of Ultrafine PM in the Los Angeles Basin and their Relation to Sources

In our previous progress report, we presented our first results on the relationship between ultrafine particle number and mass concentrations measured hourly and in 24-hour time averaged intervals. All of these data were generated in Downey. We have continued these investigation in Riverside, where we examined the relationship between the hourly ultrafine number and mass data of a given day to the hourly concentrations of EC and PAH measured by the Aethalometer. These results are summarized in Figures 20-23 and Tables 1-2. For any 24-hour period from late February to the end of March 2001 (the period for which this data analysis has been completed), the hourly ultrafine number and mass concentrations were very highly correlated, as indicated by Figures 20-21 and the results summarized in Table 1. The data in table 1 represent correlation coefficients (R^2) obtained between the hourly number and mass concentrations of ultrafine PM in a specific day.

Table 1. Correlation Coefficients (R^2) between the Hourly Ultrafine Particle Number (PN0.1), Mass (PM0.1) and Elemental Carbon (EC)

Date	PN0.1 vs EC	PN vs PM0.1
2/22/01	0.68	0.76
2/23/01	0.81	0.93
2/24/01	0.94	0.98
2/25/01	0.82	0.84
2/26/01	0.75	0.97
2/27/01	0.92	0.87
2/28/01	0.75	0.74
3/1/01	-0.27	0.93
3/2/01	-0.06	0.93
3/3/01	0.00	0.92
3/4/01	0.06	0.66
3/5/01	0.54	0.84
3/6/01	0.80	0.85
3/7/01	-0.02	0.98
3/8/01	0.36	0.69
3/9/01	0.50	0.84
3/12/01	0.95	0.96
3/13/01	0.86	0.81
3/14/01	0.72	0.56
3/15/01	0.61	1.00
3/16/01	0.21	0.92
3/17/01	0.73	0.46
3/18/01	-0.23	0.21
3/19/01	0.38	0.58
3/20/01	-0.05	0.42
3/21/01	0.84	0.60
3/22/01	-0.78	0.83
3/23/01	0.33	0.83
3/24/01	-0.66	0.96
3/25/01	-0.38	0.79
3/26/01	0.86	0.90
3/27/01	0.17	0.73
Median	0.52	0.84

The relationship between the hourly concentration of elemental carbon (EC) or PAH and ultrafine mass or number concentration was particularly revealing in identifying sources of ultrafine particles in a receptor site, such as Riverside. These results are summarized in Table 2

and also shown in Figure 22, in which the EC, ultrafine number and mass concentrations during a specific hour of the day, averaged over the 5-week period, are plotted as a function of the hour of the day.

Table 2.

<u>Time of the day</u>	<u>PM vs EC</u>	<u>PN vs EC</u>
12:00 AM	0.48	0.16
1:00 AM	0.59	0.38
2:00 AM	0.73	0.54
3:00 AM	0.74	0.66
4:00 AM	0.72	0.68
5:00 AM	0.76	0.69
6:00 AM	0.84	0.86
7:00 AM	0.83	0.75
8:00 AM	0.61	0.50
9:00 AM	0.74	0.46
10:00 AM	0.68	0.42
11:00 AM	0.64	0.19
12:00 PM	0.67	0.50
1:00 PM	0.47	-0.22
2:00 PM	0.23	-0.15
3:00 PM	0.25	-0.16
4:00 PM	0.15	-0.17
5:00 PM	0.76	0.27
6:00 PM	0.77	0.33
7:00 PM	0.83	0.77
8:00 PM	0.75	0.57
9:00 PM	0.58	0.47
10:00 PM	0.71	0.71
11:00 PM	0.60	0.52

The data plotted in Figure 22 show that the EC and PAH hourly concentrations are very well correlated. These concentrations peak during the morning traffic period (from 6 to 8 am) and decrease sharply over the course of the day. They increase again during the evening traffic period (at about 5 pm and thereafter) and remain high during the nighttime periods due to the low mixing depths and low wind speeds in the Riverside area. Local maxima during the morning traffic period and at nighttime can also be observed in the ultrafine number and mass concentrations in Riverside. However, a pronounced increase during the early afternoon period can be observed in both ultrafine PM mass and number concentrations. The ultrafine PM

concentrations start increasing right after 1 pm and become maximum at around 4 pm.[The rapid increase is particularly pronounced in the number concentrations]. The increased concentrations of ultrafine counts and mass during this period cannot be attributed to evening traffic, which does not typically start until an hour or two later than the early afternoon peak, as evident from the lower EC and PAH concentrations measured at that time of the day. Furthermore, the atmospheric mixing depth reaches its maximum during this time period, which would tend to dilute the effect of any local sources. We can only conclude from these data that the increase in ultrafine PM during the early afternoon is due to photochemical activity. It is of particular interest to compare the time trends in ultrafine counts and mass concentration in Riverside to the data shown in Figures 23- 24, obtained during two days in December 2000 and January, 2001, both of which are quite typical of the Downey data. Ultrafine number and mass concentration in Downey increase during the morning and evening traffic hours, as expected, but no mid-day peaks can be seen in their time trends over the day. These results illustrate the differences between the “source” and “receptor” sites of the Los Angeles Basin. Detailed chemical composition of ultrafine PM in Riverside, including size-fractionated samples within the ultrafine mode (described in section 7) will be presented in our next progress report.

3. Evaluation of Nitrate Sampling Artifacts of the FRM in Measuring the True PM_{2.5} Concentrations

These investigations are conducted in collaboration with the South Coast AQMD. The research objective of these studies is to determine the degree to which ammonium nitrate is lost during the 24-hr sampling period from the Teflon filters of the FRM. This study started on March 15, 2001 in Riverside and will continue through at least the end of the summer of 2001 in Rubidoux (our next Supersite site). In each intensive sampling site, the 24-hour average actual mass concentrations for PM_{2.5} (including the lost nitrate) are compared to those obtained with the FRM to determine how the differences depend on season, temperature, relative humidity, PM mass concentration and chemical composition.

The value of the sampling error or bias of the FRM will be investigated as a function of parameters such as temperature, RH and particle mass concentration. This study is currently under way and results will be presented in our next progress report.

4. Investigations of the Concentration and Source Origin of Allergens Present in Airborne Particulate Matter

The next step in the allergen project of our Supersite will be to initiate collection of PM₁₀ atmospheric particulate material at 6 Children's Health Study sites. Data obtained from the measurement of protein and analyses of allergens in the particulate matter will be useful in defining the temporal and spatial changes that can cause respiratory diseases such as allergies and asthma in populations at the Children's Health Study sites. Sampling should start soon at Atascadero (near-coastal, rural site), Glendora-San Dimas (Los Angeles Co., urban site) and Riverside (east of Los Angeles basin, down-wind of urban plume) for the first 2 months, followed by Lompoc (near-coastal, rural site), Upland (Los Angeles Co, urban site) and Mira Loma (east of Los Angeles basin, down-wind of urban plume) for 2 months. Rotation through these two groups of communities will continue during the year

Among the objectives in this Supersite project are the determinations of spatial and seasonal variations of protein and allergenic material present in airborne particulate matter in the Los Angeles area. Protein is a major component of living organisms and consequently should be a good marker for the bioaerosol content of suspended particulate matter. Allergenic proteins at nanogram levels lead to allergic disease symptoms ranging from hay fever and asthma to anaphylaxis and death – uncomfortable to serious health effects indeed.

Last quarter we reported the results of preliminary study in which we sought to assess the relative spatial distribution of airborne allergens that affect the University of Southern

California's Children's Health Study communities based on analysis of archived filters collected over the period 1994-1998. Results of that screening study showed that extractable protein levels from airborne PM₁₀-equivalent material present in the stored samples from the 13 University of Southern California (USC) Children's Health Study locations were much lower than expected, based on our earlier studies. The starting material used for the extraction of proteins was a composite of PM₁₀ -equivalent samples collected by low-volume (1.4 Lpm) sampling during 5 years (1994 – 1998) for each Children's Health Study site. Thus the low protein yields could be due to losses resulting from starting with a small amount of material or from aging and degradation during the long storage time. Never the less, it was evident from analysis of these samples that there were larger protein concentrations in the atmosphere of the eastern Los Angeles basin than in the less populated and better ventilated coastal regions.

Work during this fourth quarter period has focused on preparing for collection of larger quantities of fresh atmospheric particulate matter. Three Tisch PM₁₀ high-volume samplers, model TE6070-D, were assembled and the flow rates were calibrated using a variable orifice calibrator (TE 5028; Tisch Environmental Inc., Village of Cleves, OH) which in turn had been calibrated and certified by the manufacturer.

Field-testing of the PM₁₀ high-volume samplers was carried out at Rancho Los Amigos Hospital in Downey, CA, along with the testing of other equipment to be used for sampling during the same periods at the Children's Health Study sites. The sampling substrates, fired 8 in x 10 in quartz fiber filters, were weighed to the nearest 0.1 mg on a Sartorius model BP110S analytical balance. Uncertainties ($\pm 1\sigma$) for mass determinations were under 1.5%. In order to assess the flow rate calibrations, the particle mass collected on each filter was determined after the three samplers had run in parallel for 72 hours. The variations ($\pm 1\sigma$) for the atmospheric particle concentration ($\mu\text{g}/\text{m}^3$) determinations among the three PM₁₀ samplers were under 9%. In addition, analyses for organic carbon (OC), elemental carbon (EC) and total carbon (TC) were

carried out. The variations ($\pm 1\sigma$) for the TC concentrations among the three samplers were also under 9%.

We are most concerned at the prospect of electric utility system instability and “rolling-blackouts” during the increasing electrical energy crisis in California, which could worsen with the arrival of summer in California. The digital flow control boxes on the PM₁₀ samplers have failed due to power instability during some of the tests at Downey. Although the digital control boxes are easier to set and are more accurate than the earlier analog flow control boxes, these advantages of the digital controls would be of no use if sample collection were compromised. Therefore we have ordered and received analog flow control boxes, supplied by the manufacturer, and may decide to substitute these for the digital boxes after further testing

The next step in the allergen project will be to initiate collection of PM₁₀ atmospheric particulate material at 6 Children’s Health Study sites. Data obtained from the measurement of protein and analyses of allergens in the particulate matter will be useful in defining the temporal and spatial changes that can cause respiratory diseases such as allergies and asthma in populations at the Children’s Health Study sites. Sampling should start soon at Atascadero (near-coastal, rural site), Glendora-San Dimas (Los Angeles Co., urban site) and Riverside (east of Los Angeles basin, down-wind of urban plume) for the first 2 months, followed by Lompoc (near-coastal, rural site), Upland (Los Angeles Co, urban site) and Mira Loma (east of Los Angeles basin, down-wind of urban plume) for 2 months. Rotation through these two groups of communities will continue during the year

5. Development of a New High-Quality Continuous Coarse PM Monitor

The development and evaluation of this monitor was completed during the time periods covered by the two previous quarterly reports. A manuscript was submitted for publication to the *Journal of Air and Waste Management Association* (DEVELOPMENT AND EVALUATION OF A

CONTINUOUS COARSE (PM₁₀ - PM_{2.5}) PARTICLE MONITOR, Chandan Misra, Michael D. Geller, Pranav Shah, Constantinos Sioutas and Paul A. Solomon). Currently we are in the process of designing and further evaluating an PM10 inlet that will be used in conjunction with the continuous coarse monitor. The PM10 inlet will operate at 50 LPM and will sample isokinetically coarse particles at wind speeds varying from 2 to 24 m/s. This inlet is a modified PM10 inlet used in several FRM monitors that normally operate at a flow rate 16.7 LPM and has been modified by the USC Aerosol Laboratory to operate at 50 LPM. We are currently in the process of characterizing the inlet under controlled laboratory conditions using monodisperse laboratory-generated aerosols in the 1-10 μm size range. Following the laboratory characterization, the inlet will be characterized under carefully controlled wind speed conditions in a wind tunnel. There is a wind tunnel available at UCLA, operated by Professor W. Hinds and his group, which is however limited to wind speed up to 8 m/s. We are in the process of identifying other wind tunnels in which test can be conducted at higher wind velocities, one of which may be the US EPA facility at RTP.

6. Development of a Method for Size-dependent Chemical Composition of Ultrafine Particles

Ultrafine PM consists of primary-source particles mostly emitted by combustion associated with motor vehicles. Various studies have shown these particles to be toxic. These particles are of primary toxicological interest to our investigators of the Southern California Particle Center and Supersite since air pollutants emitted from mobile sources are the central theme of this research consortium.

Because of their lack of mass, ultrafine particles have been impossible to collect in measurable amounts over practical time intervals. Also, the very small size of these particles has prevented size distributions of them. These two problems have been solved by implementing two technologies in series. The first is the Ultrafine Concentrator (Sioutas et al., 1999), which concentrates ambient ultrafine particles from a flow rate of 220 LPM to a flow of 10 LPM by

growing them to 3-micron droplets that can be concentrated via a virtual impactor. The concentrated ultrafine PM is returned to its original size by passing through a series of diffusion dryers that remove the excess water. It is then size-fractionated and collected on filters using the second technology- the NanoMOUDI. The NanoMOUDI is a recently developed cascade impactor by Dr. Virgil Marple (University of Minnesota) that utilizes micro-orifice nozzles operating at low pressures to classify particles in five size ranges, from 180 nm down to 10 nanometers. The tandem Concentrator + NanoMOUDI system is shown schematically in Figure 25.

The entire system (concentrator + NanoMOUDI) was characterized in the laboratory. Results from the laboratory experiments are shown in Figure 26, in which the concentration enrichment, measured by means of the SMPS upstream and downstream of the USC concentrator, is plotted as a function of ultrafine particle mobility diameter. Three different types of aerosols were used; real-world indoor particles as well as laboratory-generated ammonium sulfate and ammonium nitrate ultrafine PM. The data plotted in Figure 26 clearly indicate that the concentration enrichment obtained by means of the USC concentrators was uniform throughout the 10-180 nm size range, and regardless of the type of aerosol used.

The combined USC concentrator/NanoMOUDI system was then employed in the field at two different locations (Downey and Riverside) for strict time intervals in order to collect the ultrafine particles a function of morning (rush hour), afternoon (chemical reactions/agglomeration), and evening (rush hour). The temperature, relative humidity, ambient concentrations, and enrichment factor were monitored during the course of the experiment. The filters were then weighed and analyzed for elemental/organic carbon, elements, nitrate and sulfate. Results on the size distributions as well as the chemical constituents in each size range will be presented in our next progress report, since the chemical analysis of the ultrafine samples for both locations is under way.

7. Size-segregated on-line measurement of particulate carbon and nitrate using the Integrated Collection and Vaporization Cell

The objective of our work is to provide time- and size-resolved measurements of the major chemical constituents of PM_{2.5}. Although from a regulatory point of view PM_{2.5} is considered one size class, in fact it is composed of several fractions. Particles above 1 µm are generally thought to be associated with the coarse particle mode. Many years ago, K. T. Whitby identified three modes of the ambient aerosol, “nuclei”, “accumulation” and “coarse”. The “nuclei” mode is associated with particles below 0.1 µm, the coarse mode with those above 1.0 µm. With work in the last twenty years the mid-size range, or accumulation mode has been further separated into the “condensation” and “droplet” modes, corresponding to particle from 0.1-0.5 µm and 0.5 to 1 µm respectively.

Our ICVC (integrated collection and vaporization cell) method, has provided ten-minute automated measurement of nitrates, sulfates and carbon. We are extending this method to make measurements in three size fractions. These fractions are targeted at distinguishing the condensation, droplet and coarse modes of the PM_{2.5}. We are using three cascaded ICVC cells, as described in our previous report. The analysis is done by a common analyzer that switches among the three cells.

To match the three desired size fractions, we have built cells with impaction jet diameters of 0.039 in and 0.024 in. These are cascaded above our original cell, which has an orifice of 0.0145 in. The collection efficiency of the two new cells has been measured in our laboratory using four types of aerosol: polystyrene latex, dioctyl sebacate, ammonium sulfate and ammonium nitrate. We have also tested a controlled humidification method for the newly added stages. We rely on humidification to minimize loss from particle bounce. For our single cell system, where size at the point of collection was not a concern, this was done with maximum humidification. For the size-resolved measurements, the humidity for the first two stages must be controlled and the size collection characteristics measured accordingly.

Results for Stage A ($D_j=0.039$ in) and the upper end of Stage B ($D_j=0.024$ in) are shown in Figure 27. These data were collected using an aerodynamic particle Sizer to measure the penetration of the test aerosol. While very precise, the data do not extend below the $0.5\text{ }\mu\text{m}$ lower size limit of the instrument. Most of the data were collected with a challenge aerosol of poly-disperse polystyrene latex. To avoid bounce, the collection substrate was greased. The purpose of these experiments was to characterize the cutpoint and to test the influence of the jet-to-plate spacing. While impactor design criteria often call for close jet-to-plate spacing, the in-situ analysis is best if the a larger jet-to-plate spacing can be used. Thus tests were done for spacings of 1, 2, 4 and 6 jet diameters. The results all show a cutpoint of $1\text{ }\mu\text{m}$ aerodynamic. Little degradation of the curve is seen up to 4 jet diameters. Stage A was then tested with a jet-to-plate spacing of 4 jet diameters using a liquid aerosol, dioctyl sebacate (DOS). The purpose of the liquid aerosol tests is to evaluate the efficiency of penetration of particles below the cutpoint. Data below $1\text{ }\mu\text{m}$ show penetration as good as for the solid particles. Tests were also done at 1.0 and $1.5\text{ }\mu\text{m}$ with DOS particles generated with a high-flow differential mobility analyzer. However there were particle losses in the test system that resulted in a poor balance in the counts between the upstream and downstream lines when operated without the impaction jet. We will improve our test system and repeat these experiments in the coming weeks.

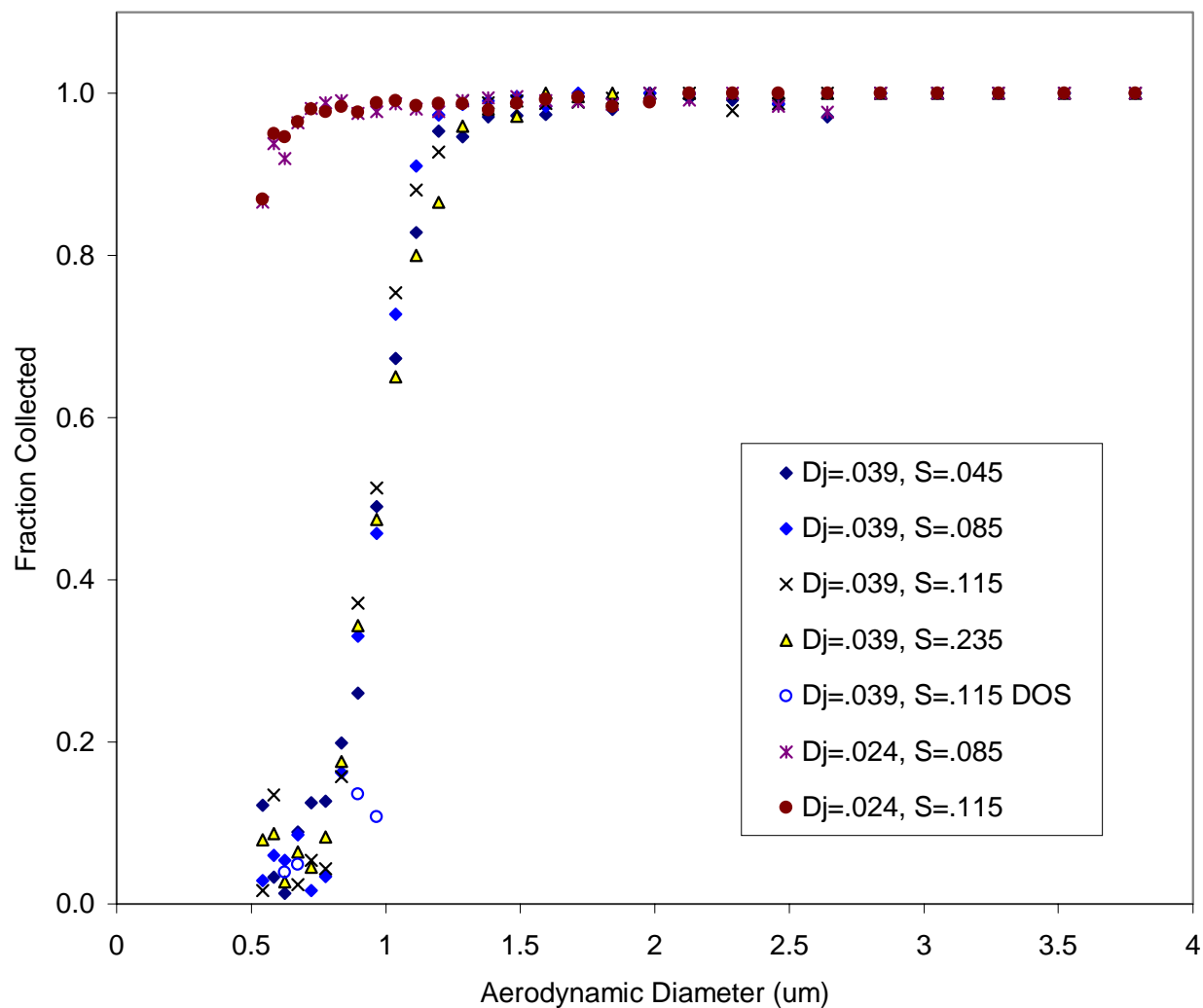


Figure 27. Collection efficiency measurements for Stage A (Dj=0.039 in) and Stage B (Dj=0.024 in) at varying jet to plate spacings. Challenge aerosol was polystyrene latex, except for one run with dioctyl sebacate (DOS) as noted. Penetration was measured using an aerodynamic particle sizer with alternating upstream and downstream counts.

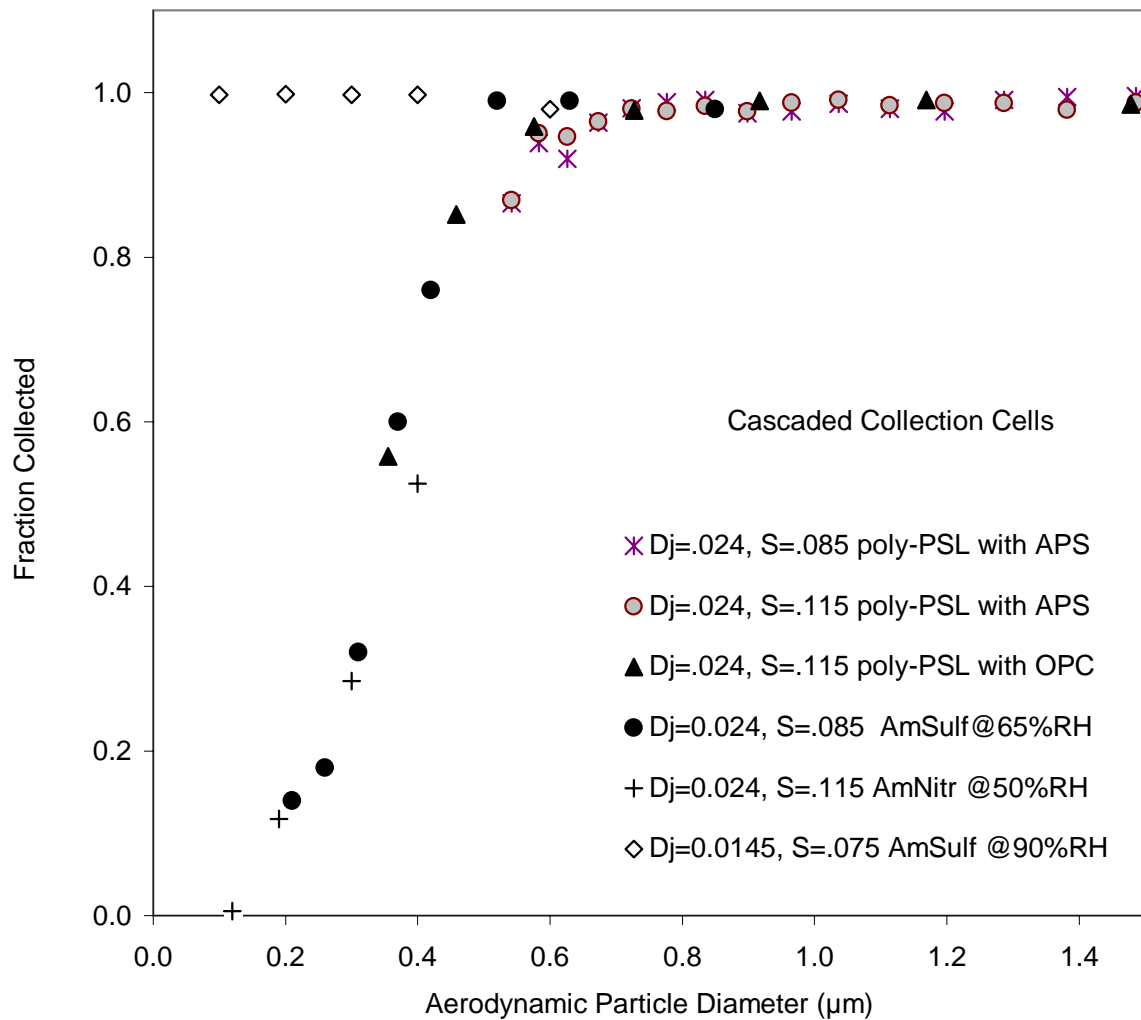


Figure 28. Collection efficiency measurements for Stage B ($D_j=0.024$ in) and Stage C ($D_j=0.0145$). Stage B was tested at two jet to plate spacings, and three types of challenge aerosol: polystyrene latex, ammonium sulfate and ammonium nitrate. Polystyrene latex penetration was measured using a polydisperse challenge aerosol with an aerodynamic particle sizer (APS) or an Climet optical particle counter (OPC) to measure the size-dependent penetration. The sulfate and nitrate tests were done using a high-flow differential mobility analyzer to generate mono-mobility particles. Efficiency was measured at the primary mobility size with simultaneous upstream and downstream counting using a condensation particle counter and a optical particle counter. For Stage C, penetration tests were done using a optical counter that had been modified for operation at low pressure.

Data for the Stage B ($D_j=0.024\text{in}$) and Stage C ($D_j=0.0145\text{in}$) are shown in Figure 28. Data are shown for three types of challenge aerosol and three different experimental configurations. Solid particle collection was done to measure the cutpoint independent of the influence of the upstream humidifier. This was done with a polydisperse mix of polystyrene latex collected onto a greased substrate. Size-dependent penetration was measured with an aerodynamic particle sizer (APS) for particles above $0.5\text{ }\mu\text{m}$ and with a Climet optical particle counter (OPC) for smaller sizes. Testing was also done with ammonium sulfate and nitrate aerosol, which had first passed through our ICVC humidifier. The relative humidity at the point of collection was either 50% or 65%, as indicated. These tests were done with a high-flow differential mobility analyzer to generate mono-mobility particles. Penetration was measured at the primary mobility size with simultaneous upstream and downstream counting using a condensation particle counter and a optical particle counter. Although some discrepancies among the different sizing systems are seen, the data show a cutpoint near $0.4\text{ }\mu\text{m}$. This is a good size for distinguishing the droplet and condensation modes. Figure 28 also shows our prior testing results for Stage C, measured at a relative humidity of 90%. This stage uses a critical orifice, with corresponding stage pressures of 0.4 atmospheres, and penetration tests were done using a optical counter that had been modified for operation at low pressure. This stage will collect material from the condensation mode and a portion of the nuclei mode.

The analytical performance of the cascaded cells has been tested with aqueous standards applied directly to the collection substrate, and with laboratory-generated challenge aerosol. Figure 29 shows calibration data for the aqueous standards. These are obtained by low-temperature flash-vaporization in a nitrogen carrier gas, with detection of the evolved nitrogen oxides using a chemiluminescent analyzer. We find nearly equal response for the two cells. The measured response is compared to that expected based on the relation:

$$Mass = \frac{MW}{MolarVolume} [Q_{anal}] Z dt$$

where MW is the molecular weight, Q_{anal} is the volumetric flow rate through the analyzer, and t is the gas phase concentration resulting from the flash analysis of the sample. For our measured analyzer flow rate of 0.65L/min, the response for 100% recovery is 36 ppbs/ng. Our experimental results are 87% and 97% recovery for cells B and C respectively.

Finally, we have tested an approach for humidification of the first two stages to a level of 65%. This is done using a nafion system with control of the absolute pressure of saturated water vapor circulated through the annular sheath of the nafion humidifier. We have tested our ability to reach 65% relative humidity with a one-foot nafion humidifier for input relative humidities of 30%, 40% and 80%. We find that this is most easily achieved through pressure control rather than flow control, and have ordered the PID controllers to automate this. For the final stage the aerosol is humidified to above 90% using a nafion humidifier with a liquid water sheath, as done previously.

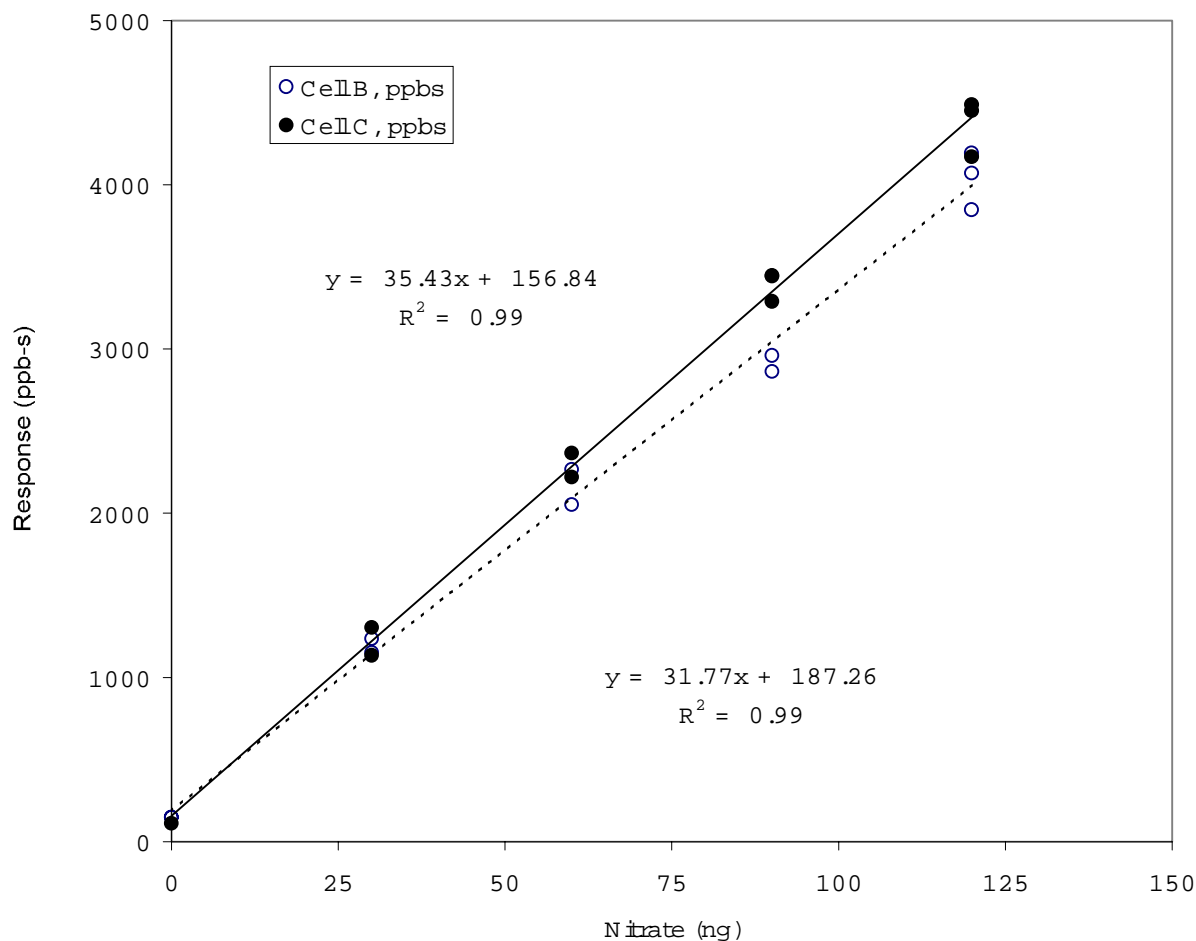


Figure 29 Measured response for aqueous sodium nitrate standards applied directly to the substrate for a two-cell cascade consisting of Cells B and C. Regression lines are shown for each cell. At the measured analyzer flow rate of 0.65 L/min the response at 100% recovery is 36 ppb-s/ng.

8. Interactions with Other Agencies and Individual Investigators.

The data that have already been-(or will be) generated by our Supersite have already become a valuable resource for a variety of agencies and individual investigators. These interactions and collaborative activities are summarized in the following paragraphs.

The California Energy Commission requested our 24-hour averaged PM_{2.5} and PM₁₀ mass concentration data at Downey during the period of October 2000-January 2001. These data will be used in conjunction with model predictions to determine the appropriateness of building a power plant in the Downey area and the degree to which the new plant will contribute to the overall PM₁₀ mass concentration in that area.

The California Air Resources Board (CARB) and the South Coast AQMD will contribute about \$200,000 for a three year period, starting in the fall of 2001, for a field monitoring study in which the Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc.) and low temperature TEOM (TEO 1400A, R&P Inc.) will be deployed in three of the Children's Health Study (CHS) at a time for a period of 3 years. Of that amount, about \$120,000 will be covered by the ADMQ through funds offered by EPA's region IX to assist the LA Supersite program. CARB will cover the remaining \$80,000 and has already available instrumentation of about \$350,000 to support this study. The proposed activities will make it possible for the first time in the air pollution history to generate unique data on the properties of ultrafine particles in near-continuous time intervals and in 3 several locations of the LA Basin at a time. The deployment of these new air-monitoring technologies will improve what is known about the nature of ultrafine, PM₁ and PM₁₀ particulate matter in the USC Children's Health Study (CHS) communities and thus provide unique exposure data that will be readily linkable to ongoing health studies and of direct use in assessing the association between respiratory health and ambient particle exposure. Furthermore, the deployment of SMPS would provide investigators of the Southern California Particle Center with unique data on the size distributions of fine and ultrafine PM in "source" and "receptor" sites of the LA Basin, which will be essential in developing and validating predictive models on PM formation and transport mechanisms in the Basin. This will be accomplished by monitoring in real-life, PM formation and growth as the urban PM plume moves along predominant air trajectories, such as the "nitrate" or the "vehicle" trajectory.

Finally, two proposals were submitted to the EPA STAR program and the National Institute of Health, respectively, that will make use of the LA Supersite data. The objective of the EPA

STAR proposal, led by Dr. Jack Harkema (Michigan State University) is to conduct atmospheric and toxicologic research designed to understand the adverse effects of airborne particulate matter (PM) of various size fractions (coarse, fine, and ultrafine particles) on airways with allergic airway disease. An integrated investigative team of environmental and biomedical scientists from Michigan State University (MSU) and the Southern California Particle Center and Supersite (SCPCS) will conduct atmospheric and toxicologic research at three Supersite sites in the Los Angeles Basin, each of which have distinct air-pollution profiles. Physico-chemical analysis of particles and co-pollutants in that study will be provided by the LA Supersite. The NIH proposal, led by Dr. Ralph Delfino (UC Irvine), will make use of the LA Supersite data generated in Boyle Heights (source site) and Riverside/Rubidoux (receptor sites) to investigate the whether personal exposure to particulate air pollution interact with or explain the effects of NO₂ on asthma morbidity.

9. Progress on Site identification and Deployment of the PIU

A key feature of our Supersite activities was the ability to conduct state-of-the-art measurements of the physicochemical characteristic of PM in different locations of the Los Angeles Basin (LAB). We have proposed a 2.5-year repeating cycle of measurements at five locations. Each location will be sampled during a period of intense photochemistry (defined approximately as May – October) and low photochemical activity (defined as the period between November – April). In our previous report, we mentioned that all sites except of the Claremont/Upland site were identified and secured. In early March 2001, we identified and secured our last site in Claremont. The site is property of the Southern California Water Company and it is ideally located in the foothills of the San Bernardino Mountains, right along the “vehicle-oriented” trajectory. The site has ample power readily available to support our PIU as well as our PM center activities.

Sampling in our Rancho Los Amigos has been completed. Sampling in Riverside started during the 3rd week of February 2001. We anticipate staying in Riverside until the end of May, 2001,

by which time we will move to Rubidoux for the months of June, July and August 2001. Starting September 2001 we will move to Claremont/Upland, where we will spend the next 4-5 months. Finally, in the winter of 2002 we will move to Azusa. It should be noted that this is a tentative plan and it may be subject to changes, depending on the needs of our PM Center investigators who will be using these data.

Consistent with our original proposal, we have just started the freeway study and the characterization of PM and gaseous co-pollutants as a function of distance from a freeway. Sampling (concurrently with animal exposures) at USC started during through last week of April 2001. The main campus of USC is our upwind site, as it is located more than 1 mile to the west or south of freeways 110 and 10, respectively. Over the next 4-5 months, measurements will be taken in our site in Boyle Heights, which is downwind of Freeway 5 and is located 15-20 meters away from the freeway. Additional PM and copollutant measurements will be taken in discrete distances and perpendicularly to Freeway 5, in conjunction with inhalation exposure studies to concentrated PM from the freeway, utilizing the USC particle concentrators. We anticipate that we will have our first results presented in our upcoming progress report.

10. Progress with Quality Integrated Work Plan (QIWP) and Data Management

Our Quality Integrated Work Plan (QIWP) was submitted originally to EPA on January 31, 2001. In its response, EPA recommended minor revisions, which were incorporated into our final version, which was sent on April 21, 2001 to the Office of Air Quality Planning and Standards Emissions, Monitoring and Analysis Division for final approval. On May 1, 2001, we received notification from EPA that our QWIP was approved.

In addition to the revised QIWP, we have completed a data management manual specific for the Southern California Supersite. The manual covers all the essential subjects of the QWIP, and

details how to transmit our Supersite dataset into the NARSTO format for permanent archiving in NASA.

During this period, we also used the EC/OC concentrations of the Aethalometer as a model dataset to test transmission of our Supersite datasets to NARSTO. We used the most updated version of NARSTO transmission template (NARSTO 2001/04/23 (2.208)) to construct a transmission dataset by using one-day Aethalometer data. The transmission dataset was sent to the data management staff of NARSTO for review. Upon final approval, the datasets obtained from different PIU instruments will be prepared and officially submitted to the NASTO Permanent Database Archive starting in May 2001.

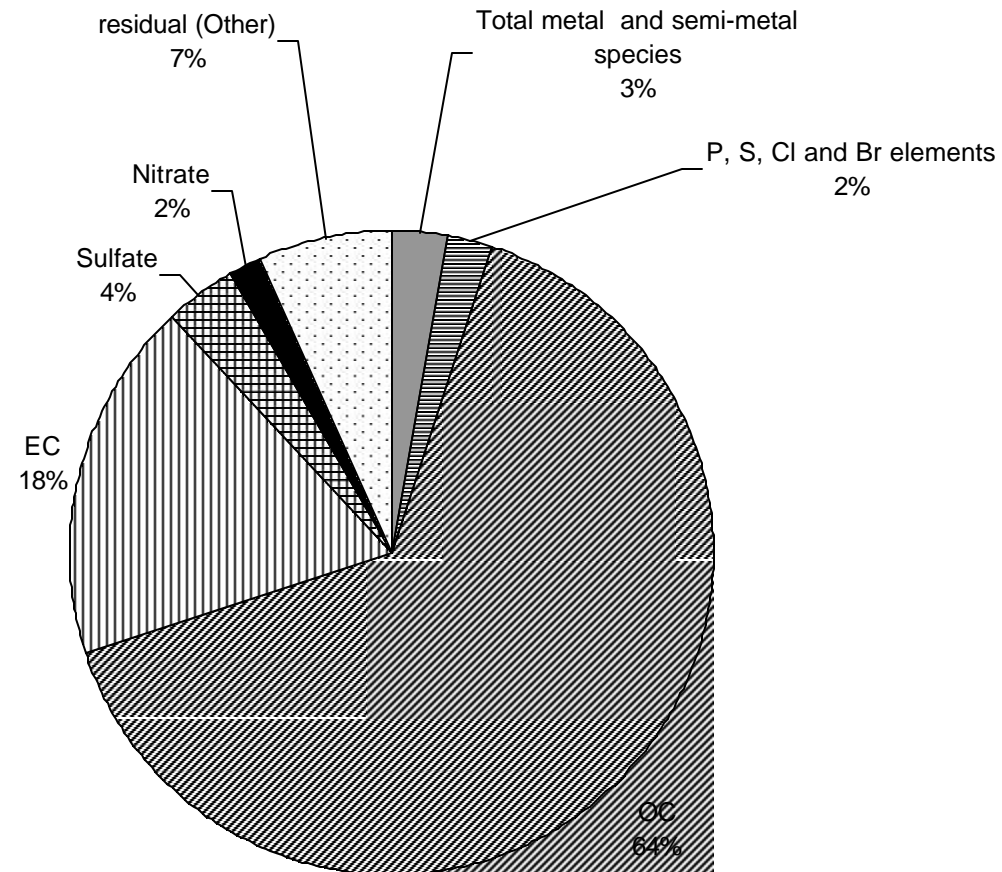
11. References

Luhrman, F.W., Wexler, A.S., Pandis, S.N., Musarra, S., Kumar, N., and Seinfeld, J.H. (1997). Modeling urban and regional aerosols-II. Application to California's South Coast Basin. *Atmospheric Environ* 31:2695-2715

Sioutas, C., Kim, S., and Chang, M. "Development and evaluation of a prototype ultrafine particle concentrator." *Journal of Aerosol Science*, 30 (8):1001-1012, 1999.

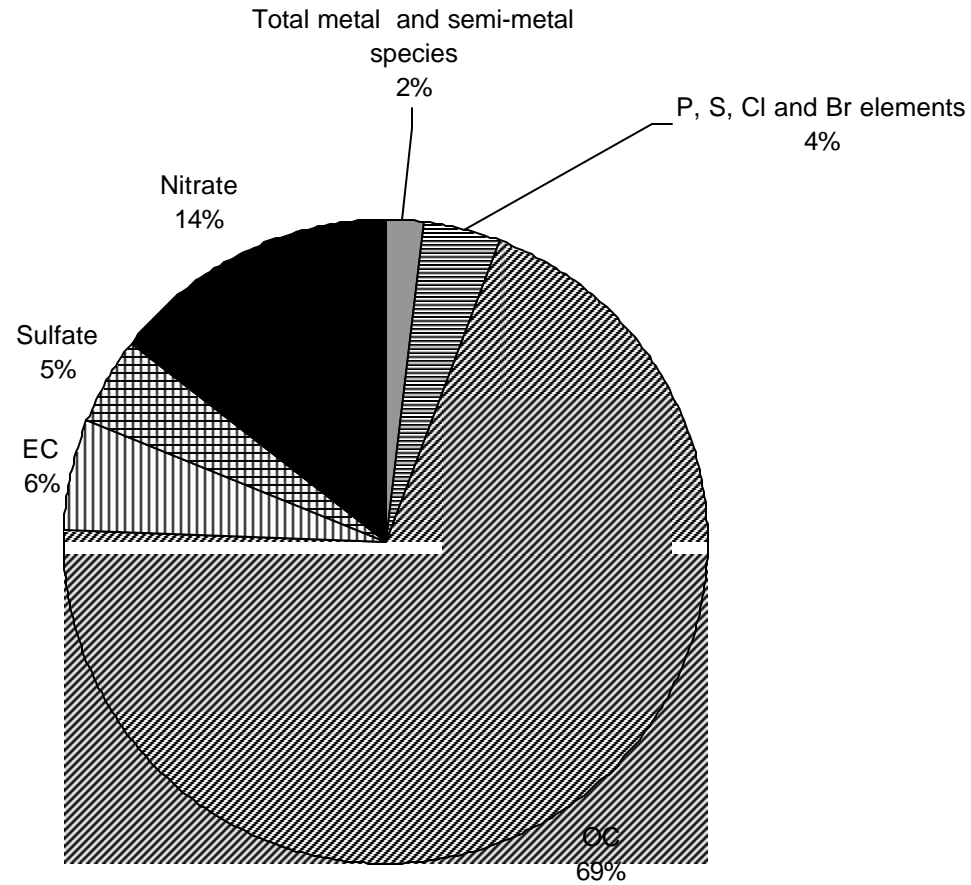
Misra, C., Geller, M., Sioutas, C and Solomon P. "Development and evaluation of a continuous coarse particle monitor". Manuscript submitted for publication in *Journal of Air and Waste Management Association*, January 2001

24 hour Average mass balance of particulate matter (0-0.1 um) measured with MOUDI, in Downey, CA from 10/03/00 to 1/25/01



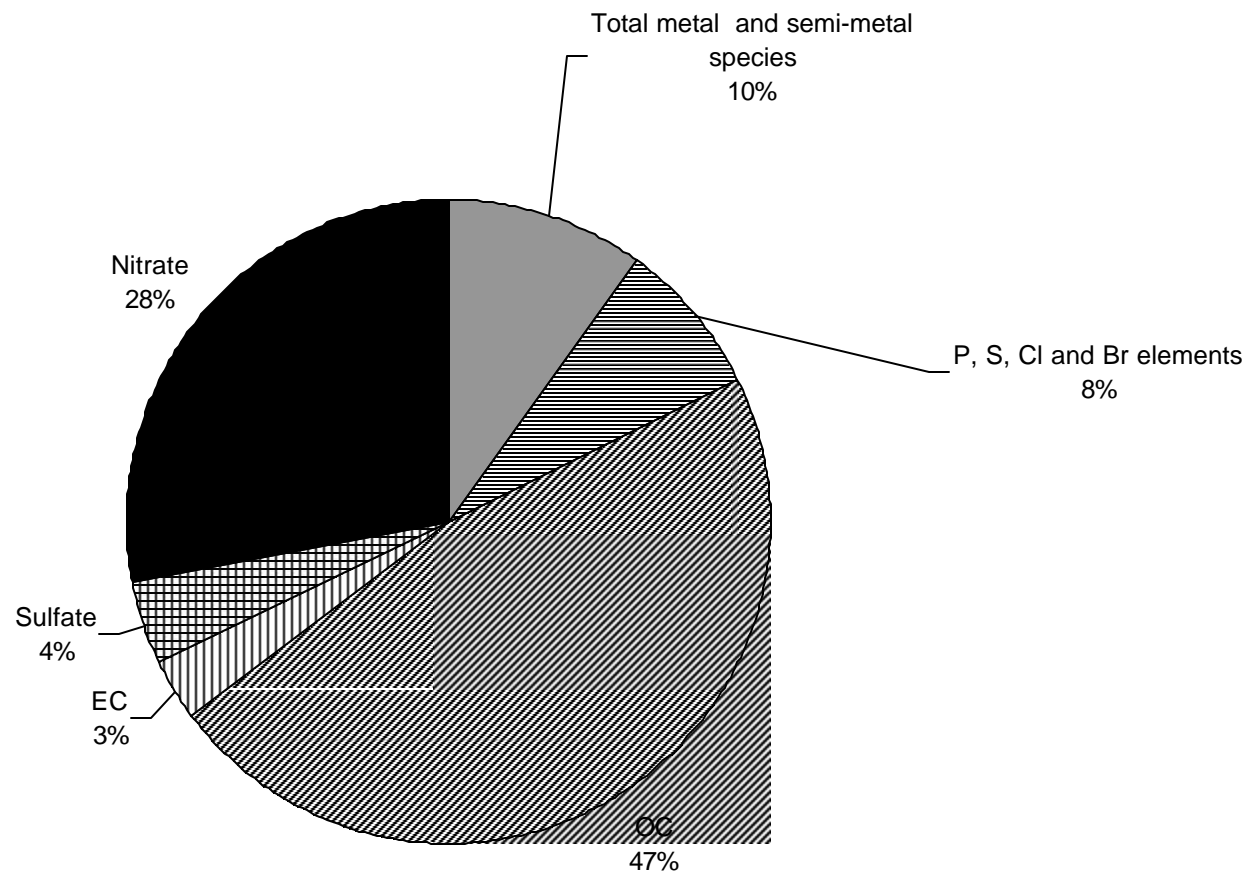
Residual is the filter mass minus total chemical masses (total filter mass = 4.224 ug/m3).

24 hour Average mass balance of particulate matter (0.1 - 0.32 μm) measured with MOUDI, in Downey, CA from 10/03/00 to 1/25/01



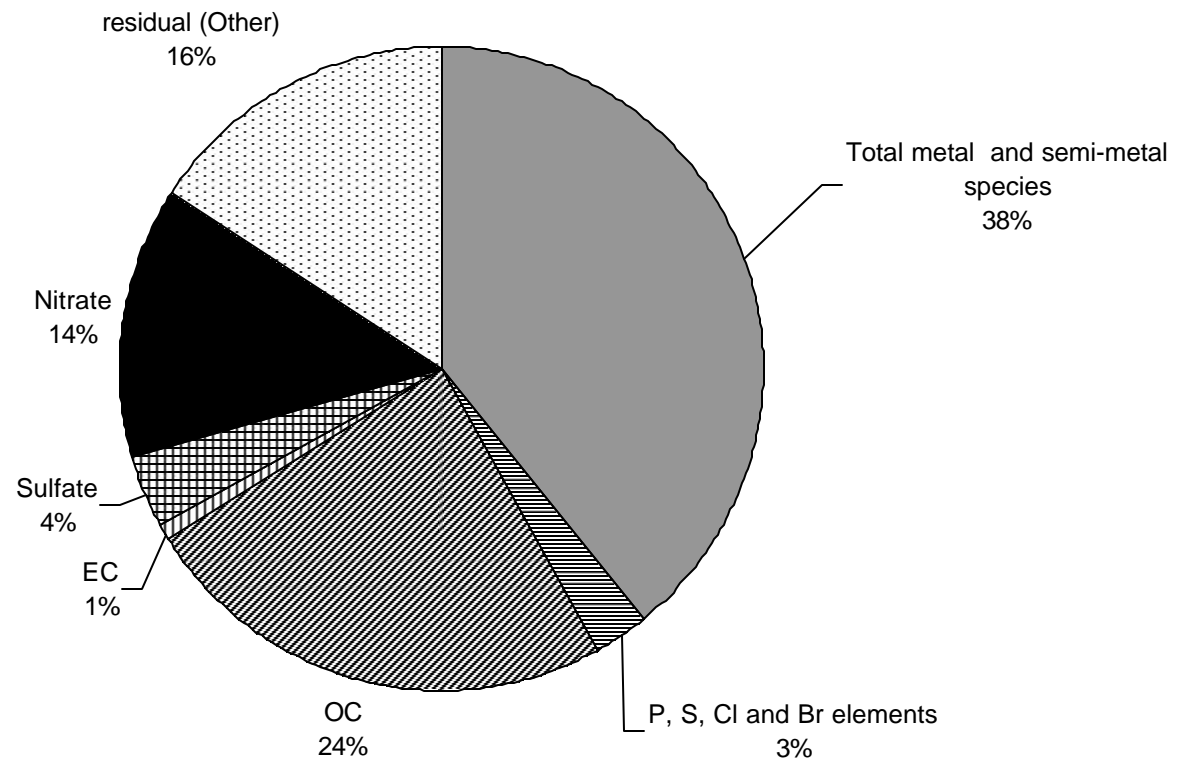
Residual, the filter mass minus total chemical masses, was negative in this particle size (-1.224 $\mu\text{g}/\text{m}^3$ out of total filter mass, 9.061 $\mu\text{g}/\text{m}^3$).

24 hour Average mass balance of particulate matter (0.32 - 1.0 μm) measured with MOUDI, in Downey, CA from 10/03/00 to 1/25/01



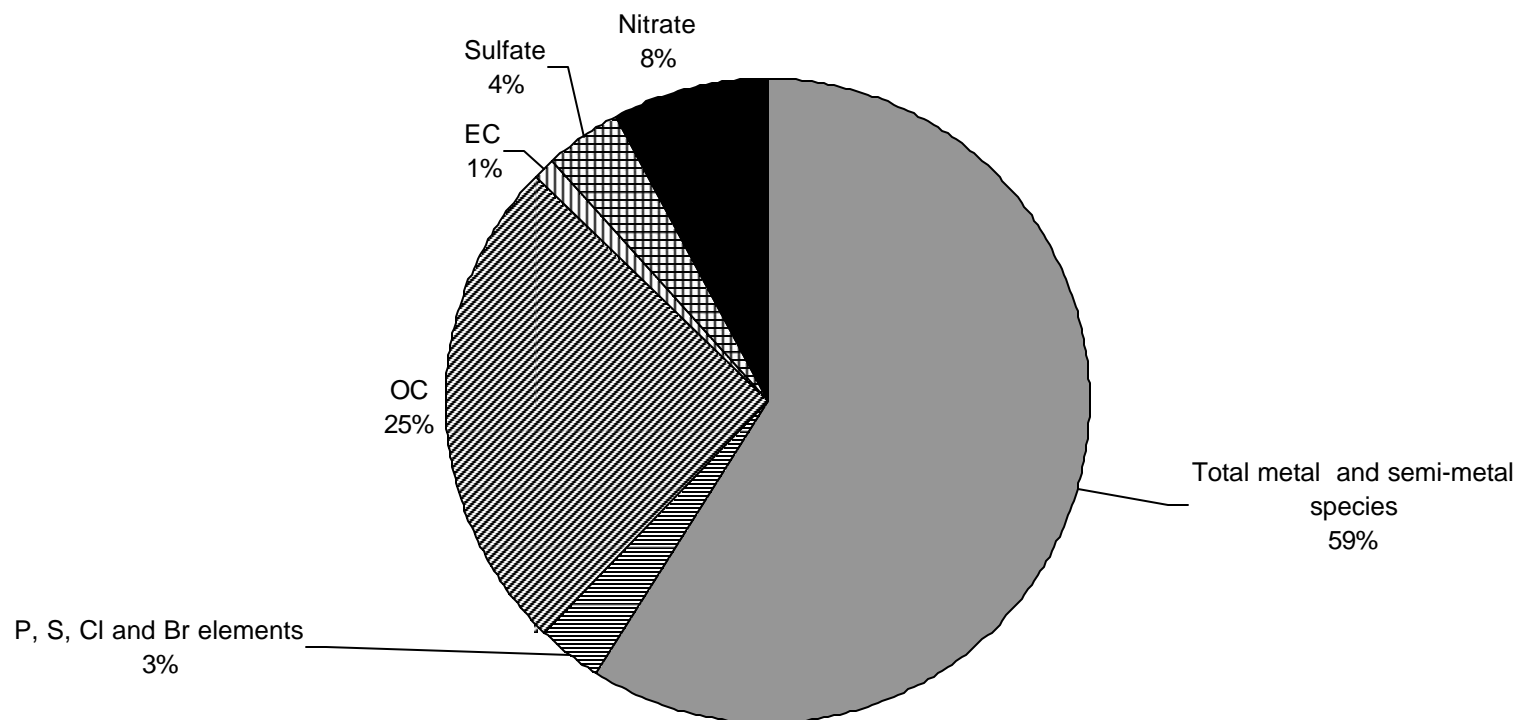
Residual, the filter mass minus total chemical masses, was negative in this particle size (-1.273 $\mu\text{g}/\text{m}^3$ out of total filter mass, 7.696 $\mu\text{g}/\text{m}^3$).

**24 hour Average mass balance of particulate matter (1.0 - 2.5 μm) measured with MOUDI, in
Downey, CA from 10/03/00 to 1/25/01**



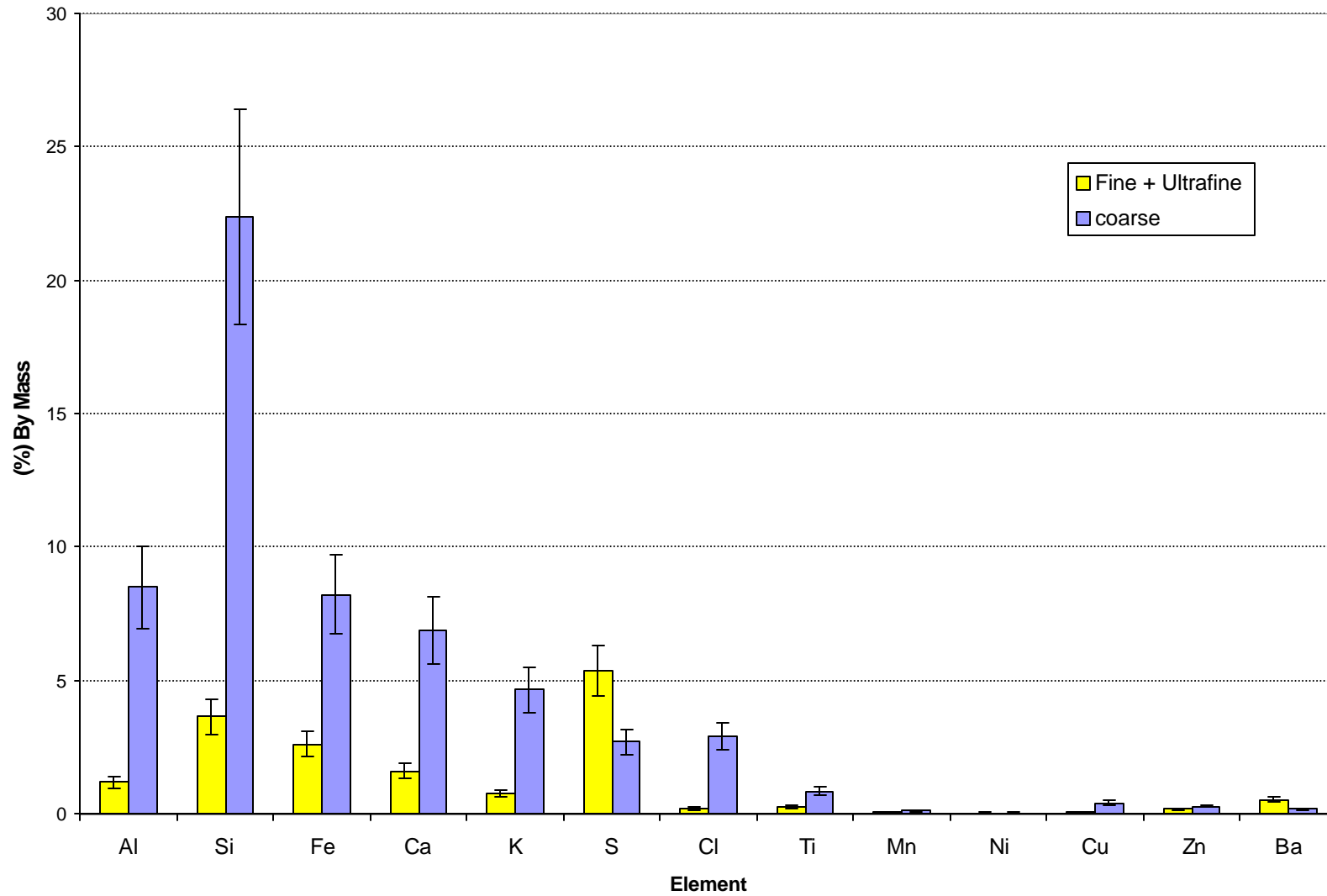
Residual is the filter mass minus total chemical masses (total filter mass = 5.327 $\mu\text{g}/\text{m}^3$)

**24 hour Average mass balance of particulate matter (2.5 - 10 μ m) measured with MOUDI, in
Downey, CA from 10/03/00 to 1/25/01**

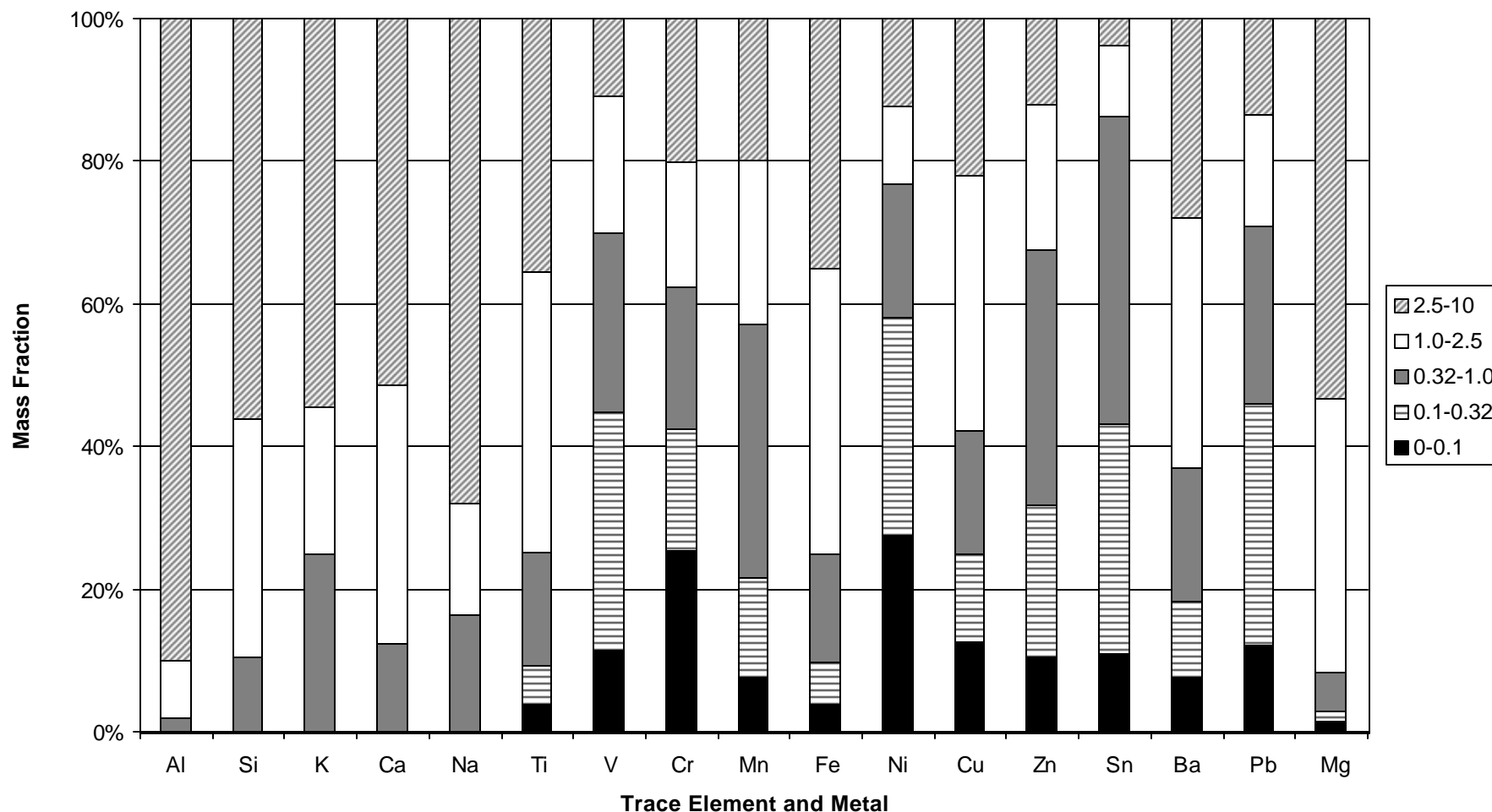


Residual, the filter mass minus total chemical masses, was negative in this particle size (-0.073 μ g/ m^3 out of total filter mass, 6.656 μ g/ m^3).

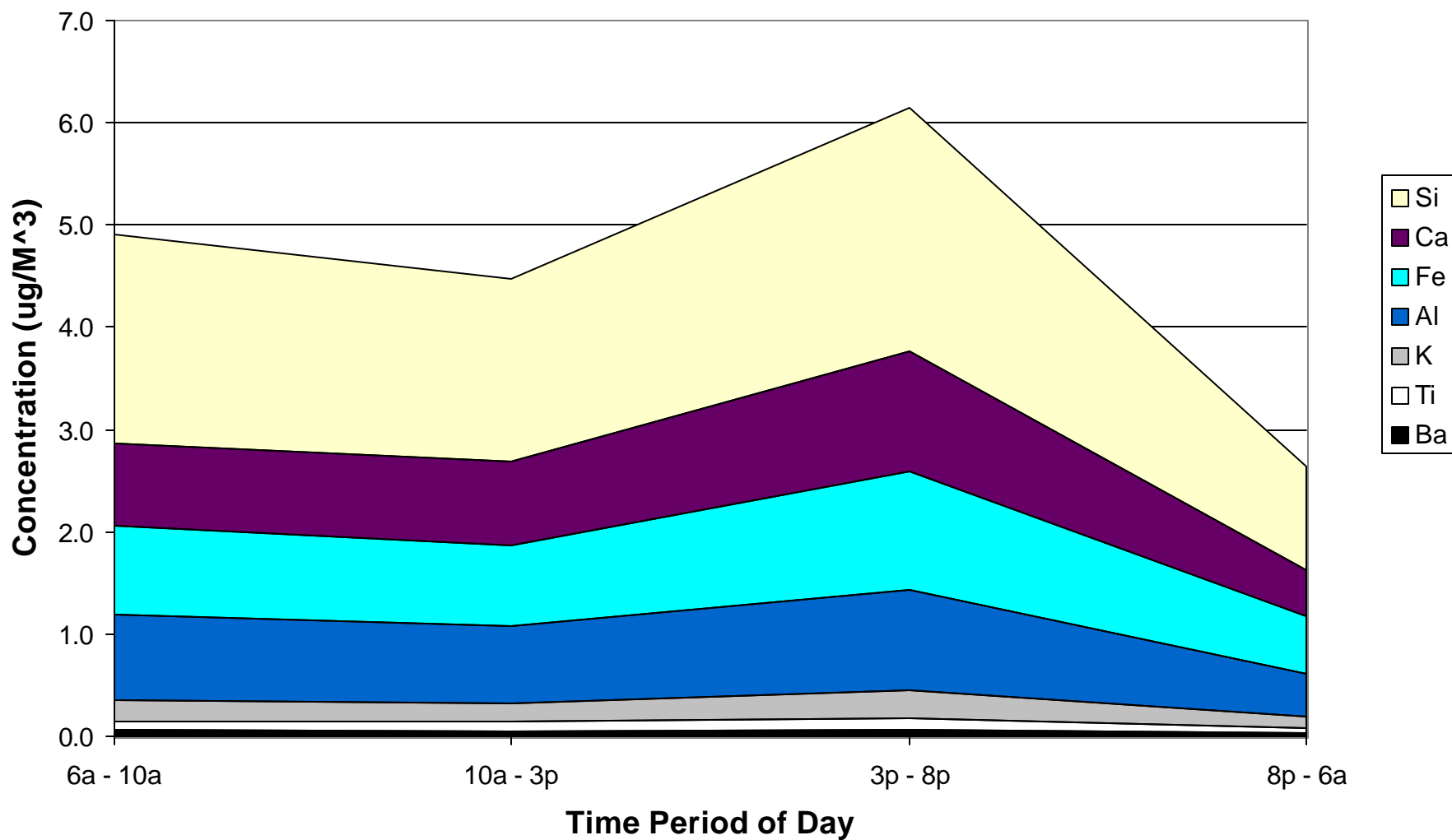
Elemental Composition of Fine and Coarse Particles



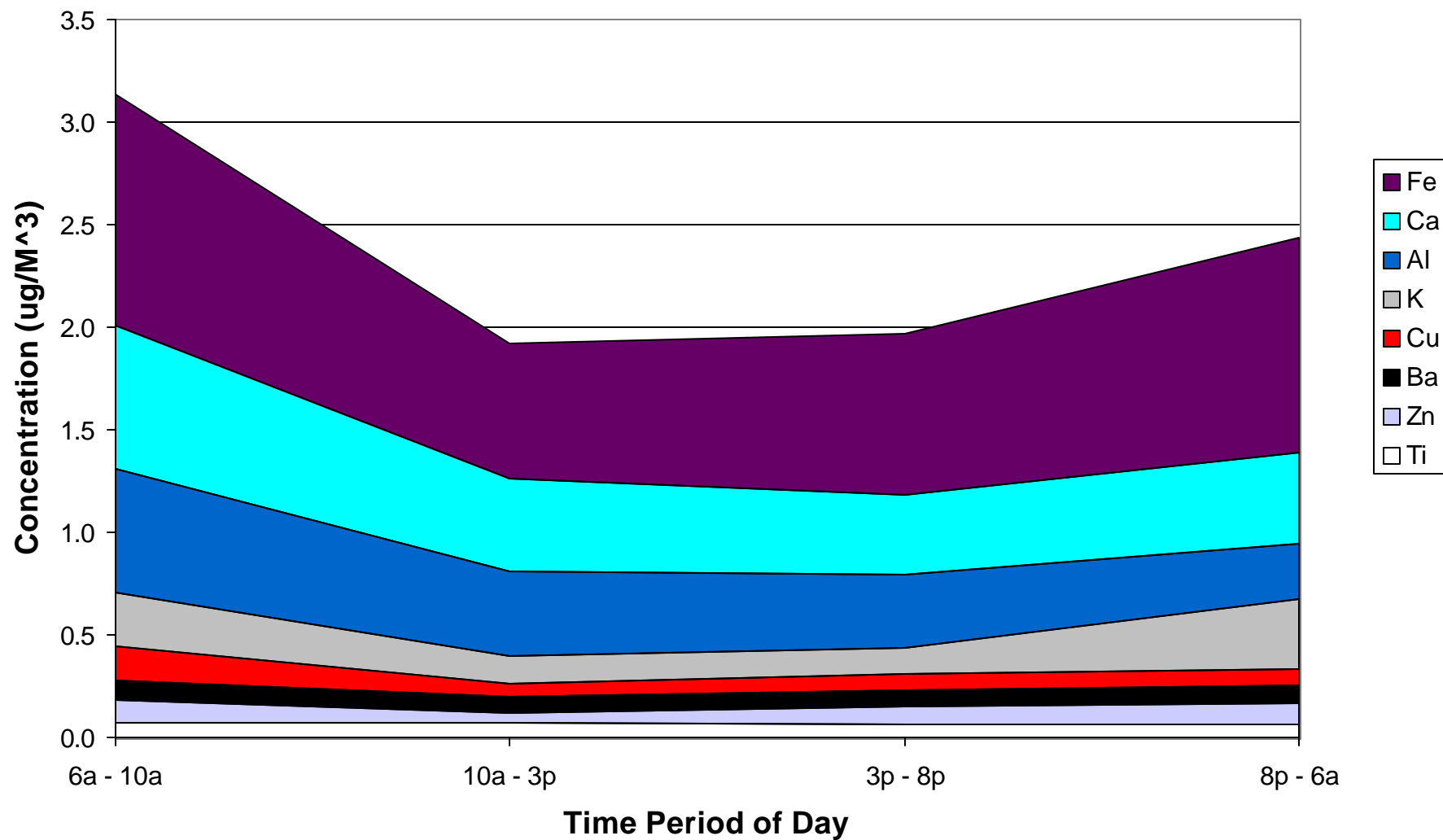
Average Mass Fraction of Trace Elements and Metals in 5 Particle Size Ranges. Based on Sixteen 24-hr Averaged Tests from October 3, 2000 to February 1, 2001. Location: Downey, CA



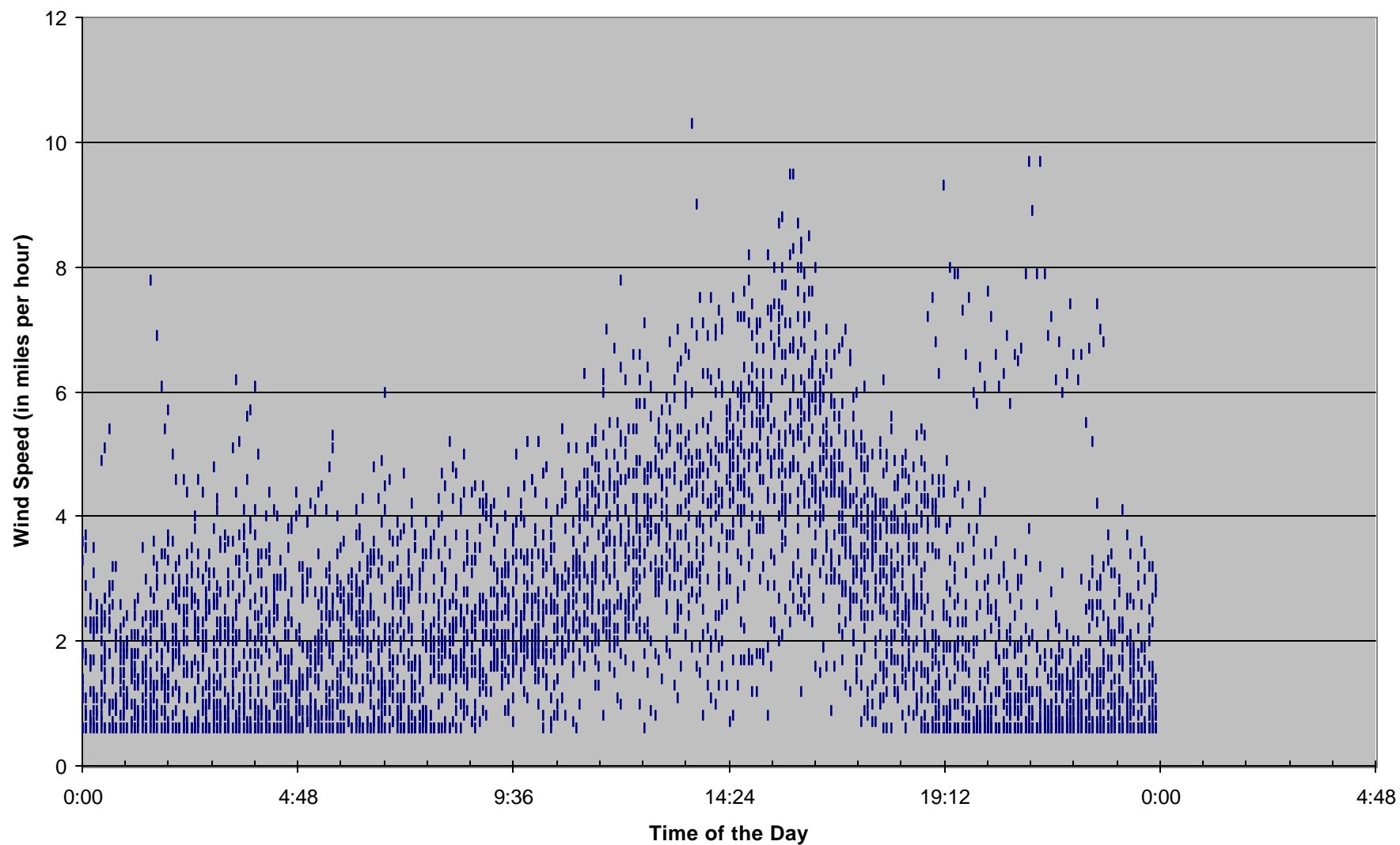
**Coarse PM Metal Elements for 4 time Periods of 9 Different Days between
Dec 1, 2000 and Feb 1, 2001; Downey, CA**



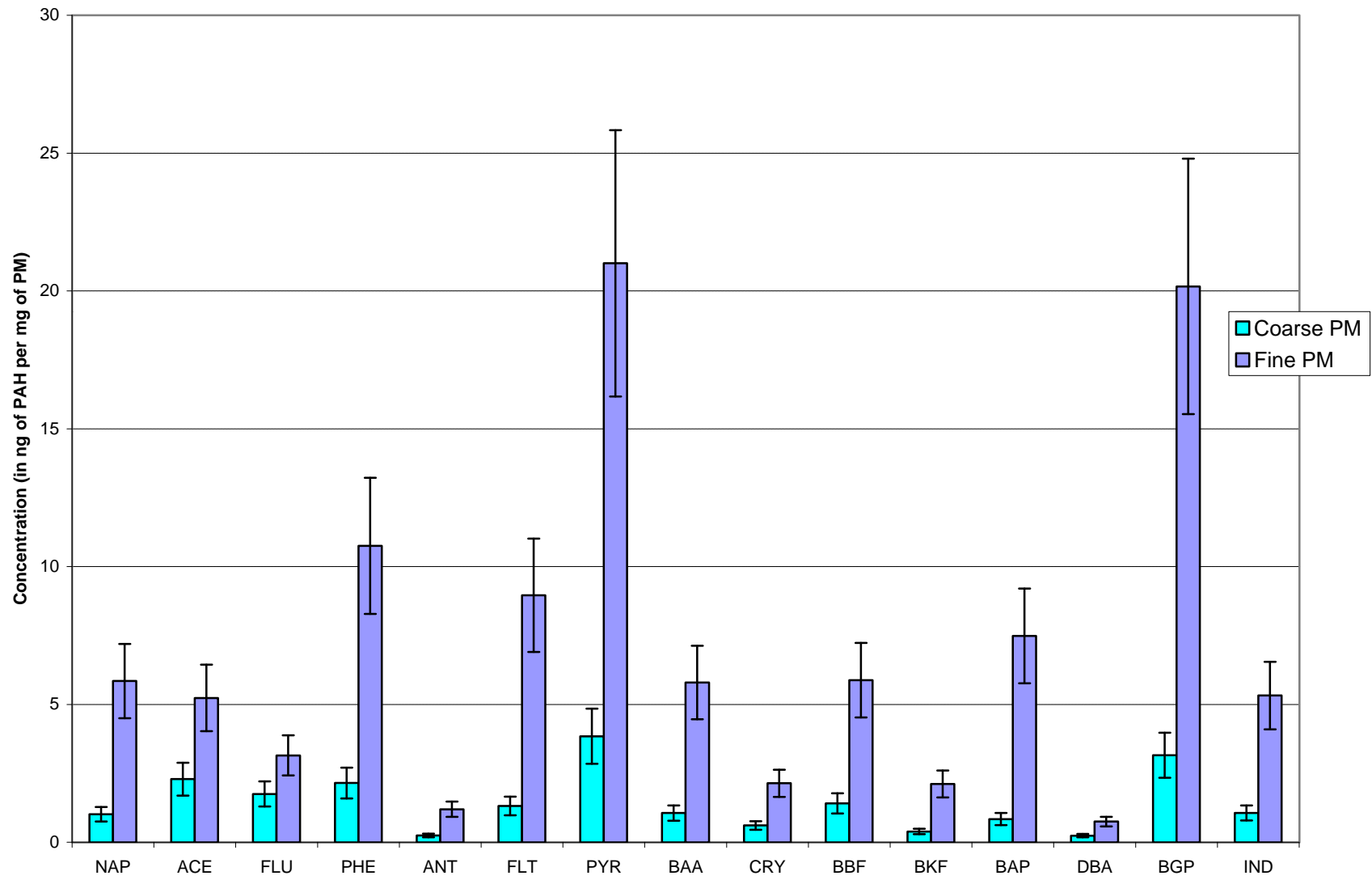
**Fine PM Metal Elements for 4 time Periods of 9 Different Days between
Dec 1, 2000 and Feb 1, 2001; Downey, CA**



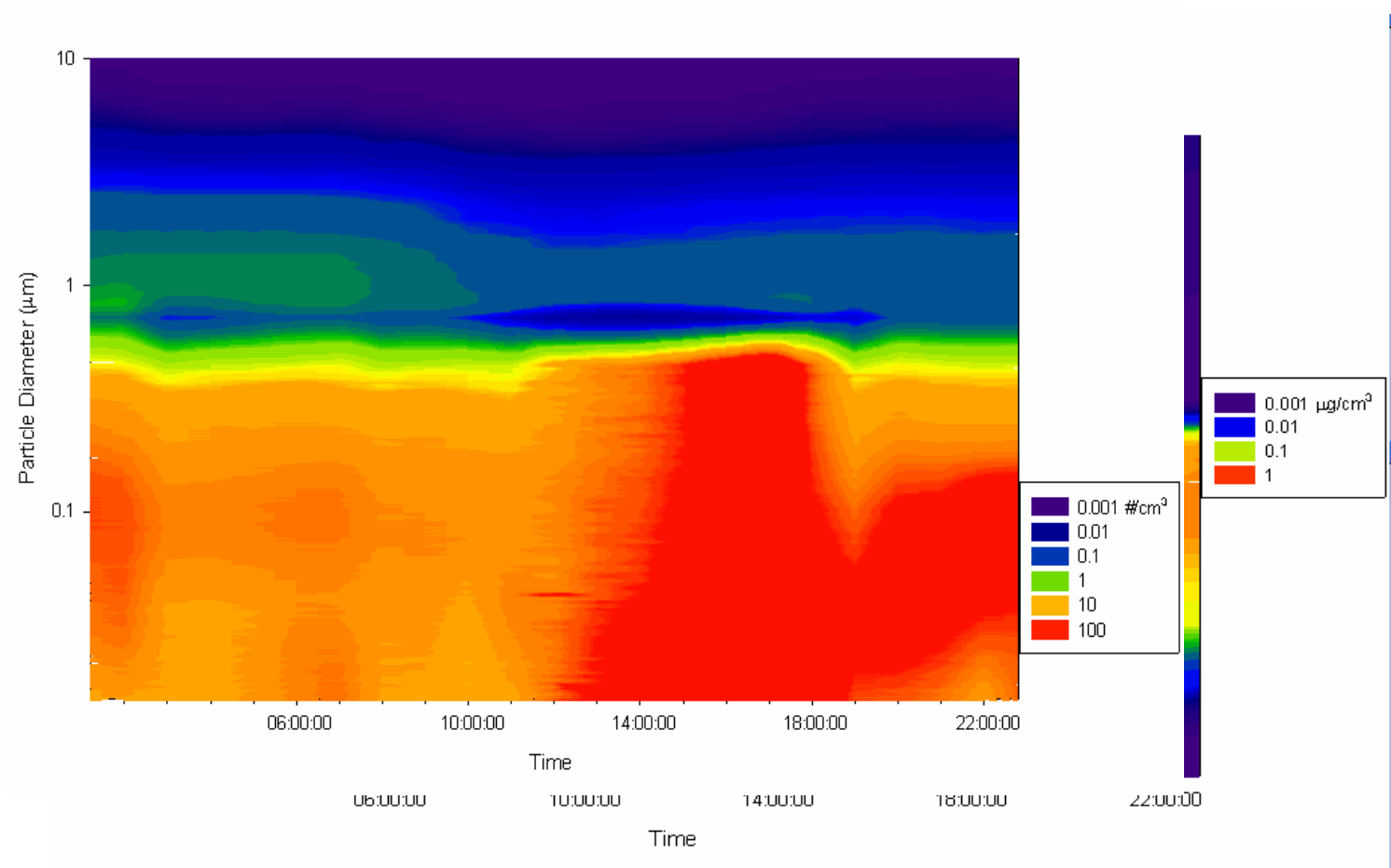
Wind Speed vs Time of the Day. Downey, CA



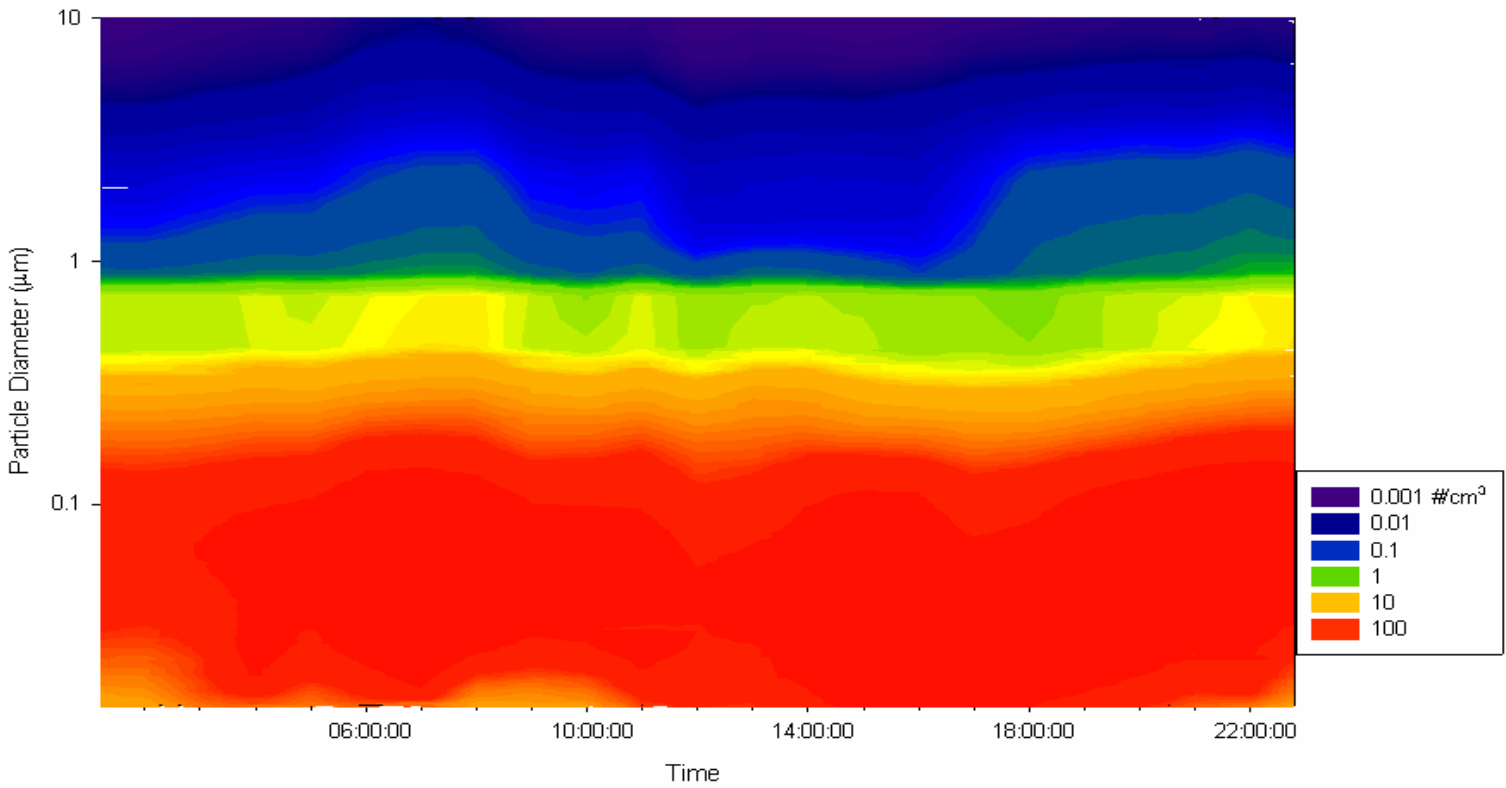
PAH Concentration in Coarse and Fine Particles



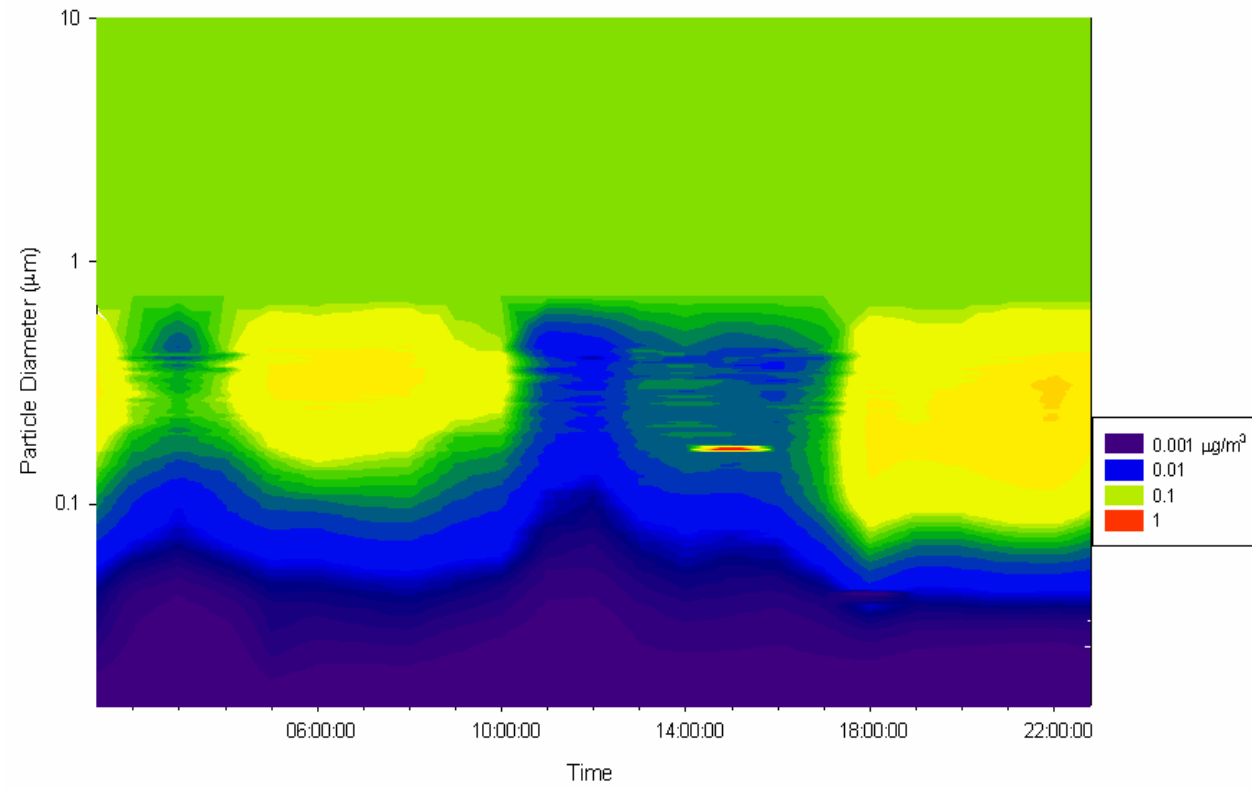
Contour Graph For Ambient Particle Size Distribution
at Riverside at 3/3/01



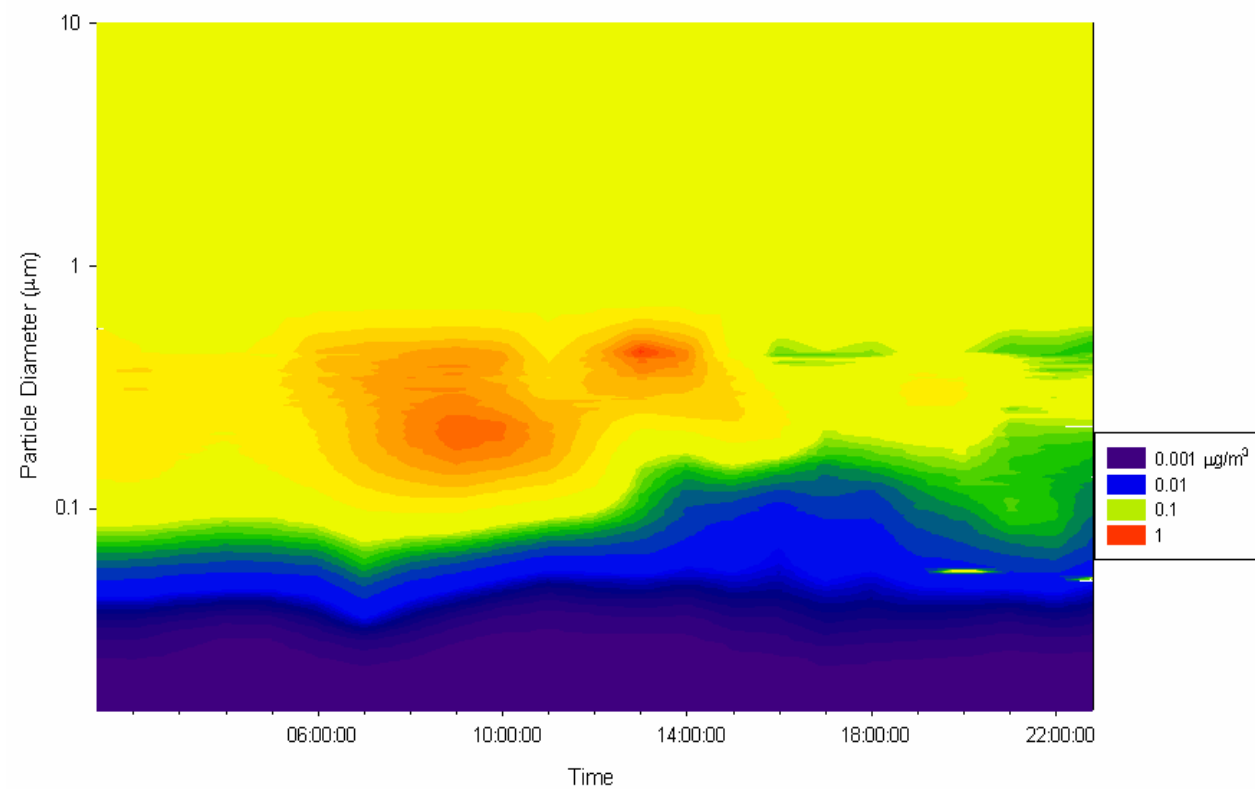
Contour Graph For Ambient Particle Size Distribution
at Rancho at 02/02/01



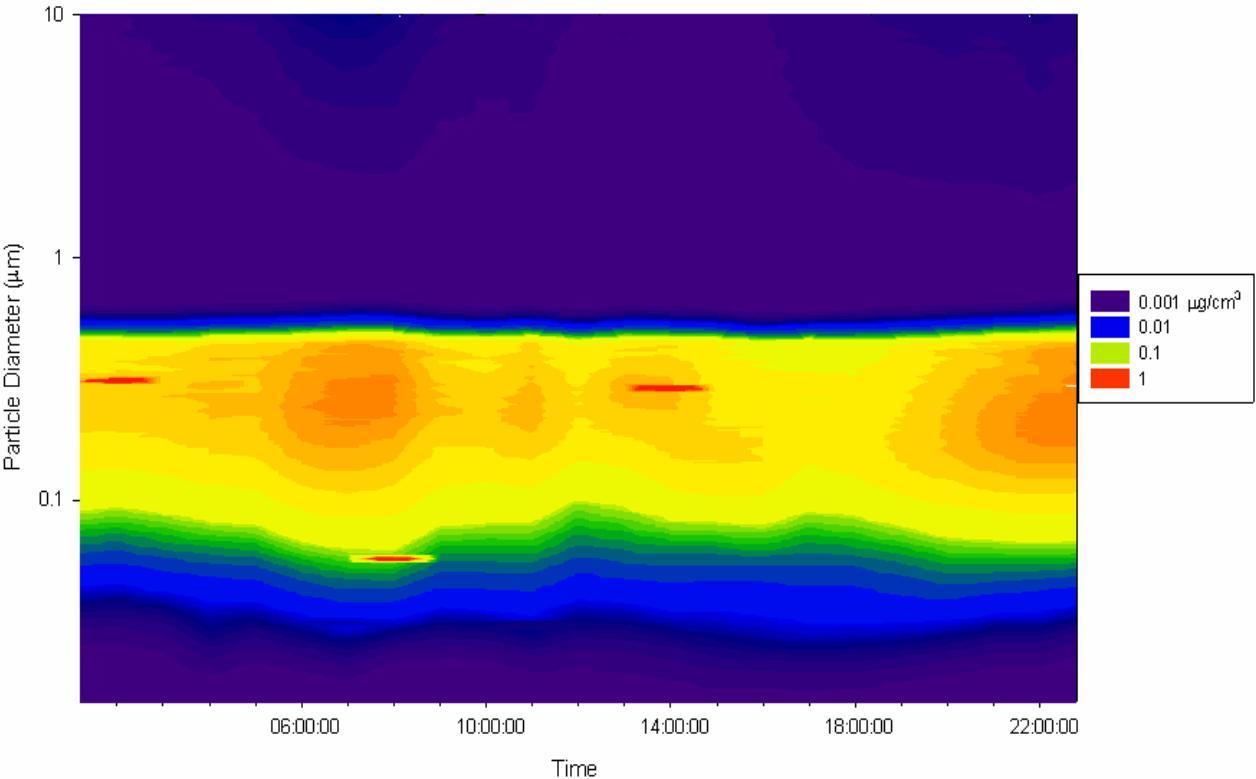
Contour Graph For Ambient Particle Mass Distribution
at Riverside at 2/27/01



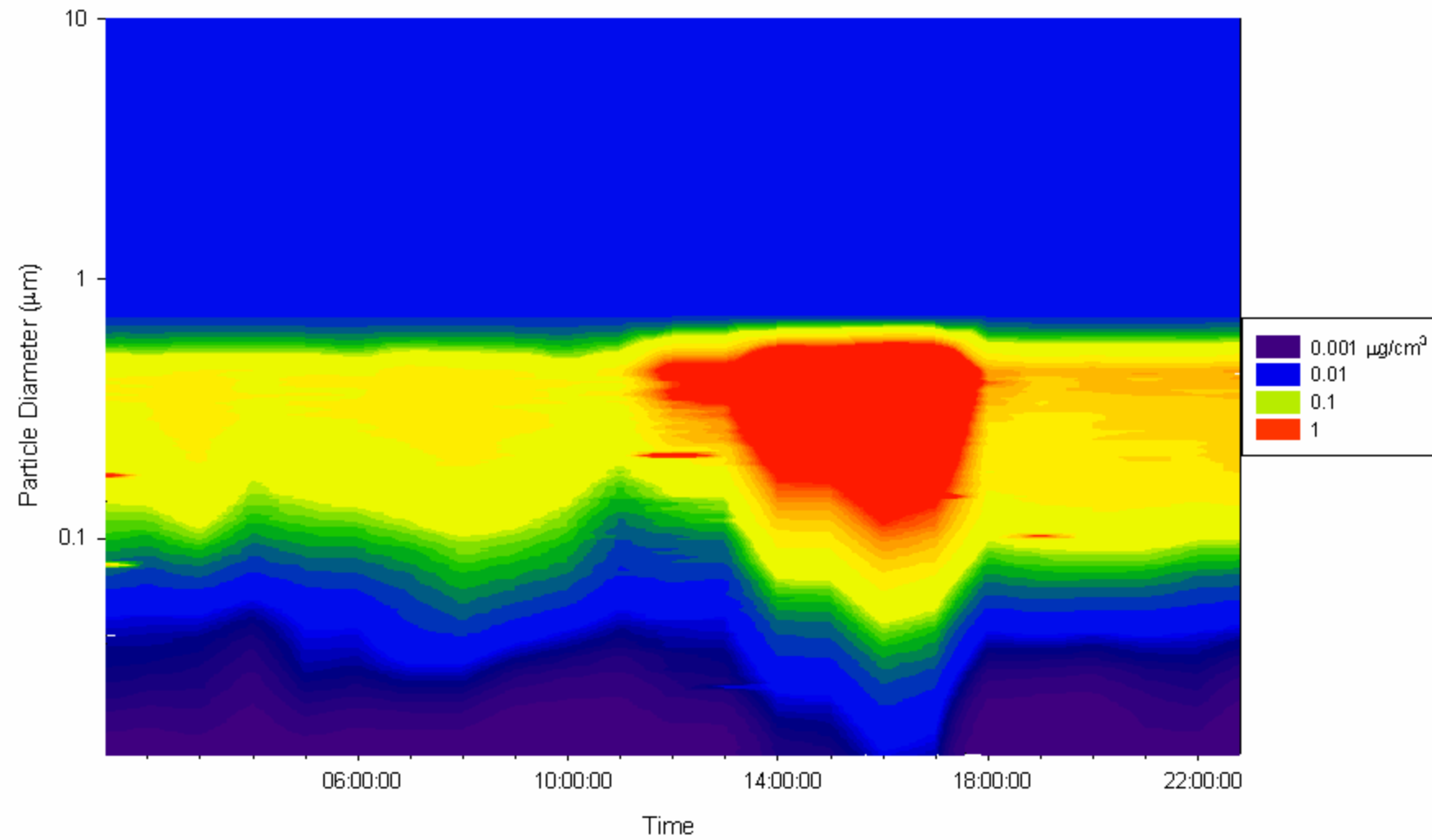
Contour Graph For Ambient Particle Mass Distribution
at Riverside at 2/22/01



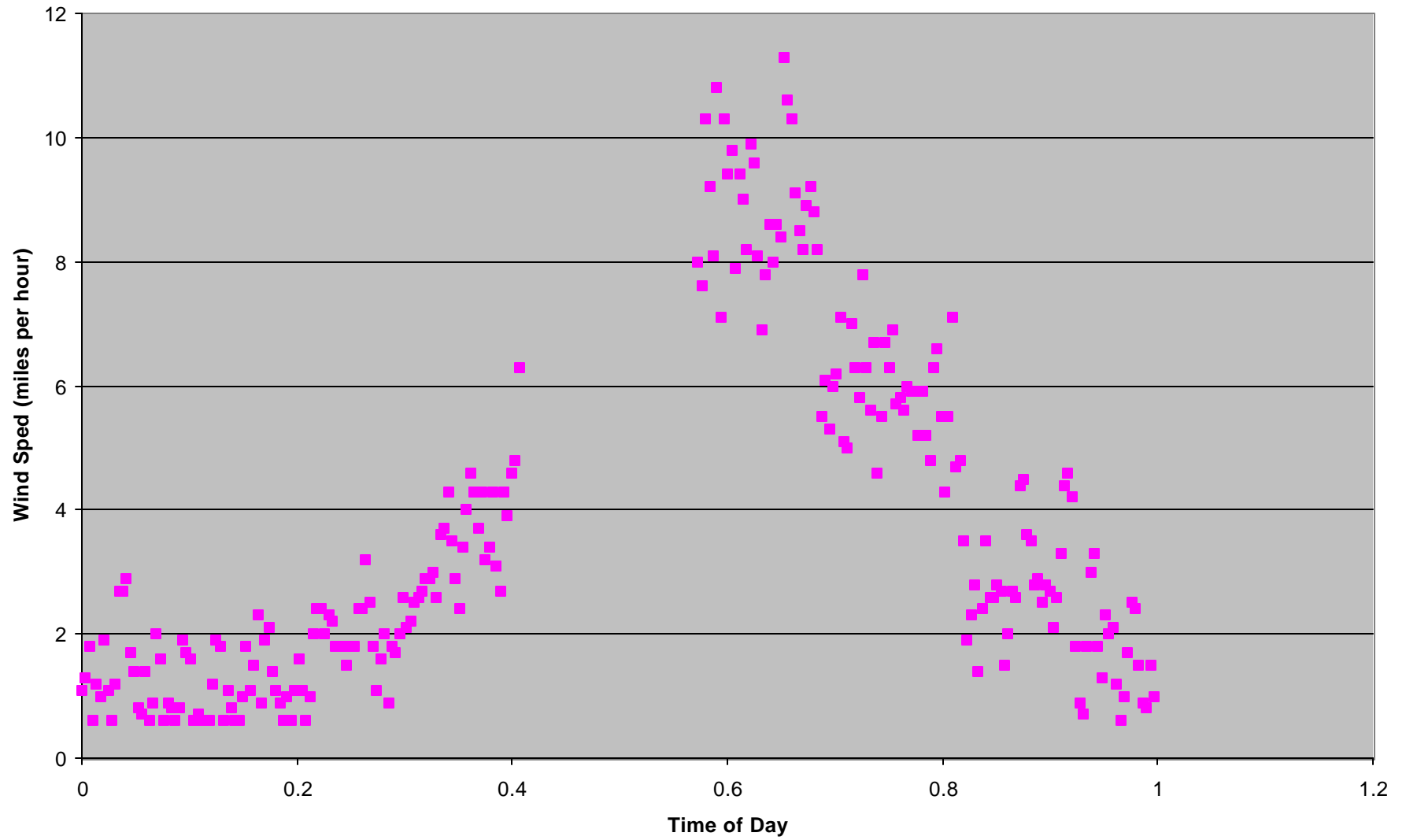
Contour Graph For Ambient Particle Mass Distribution
at Rancho at 02/02/01



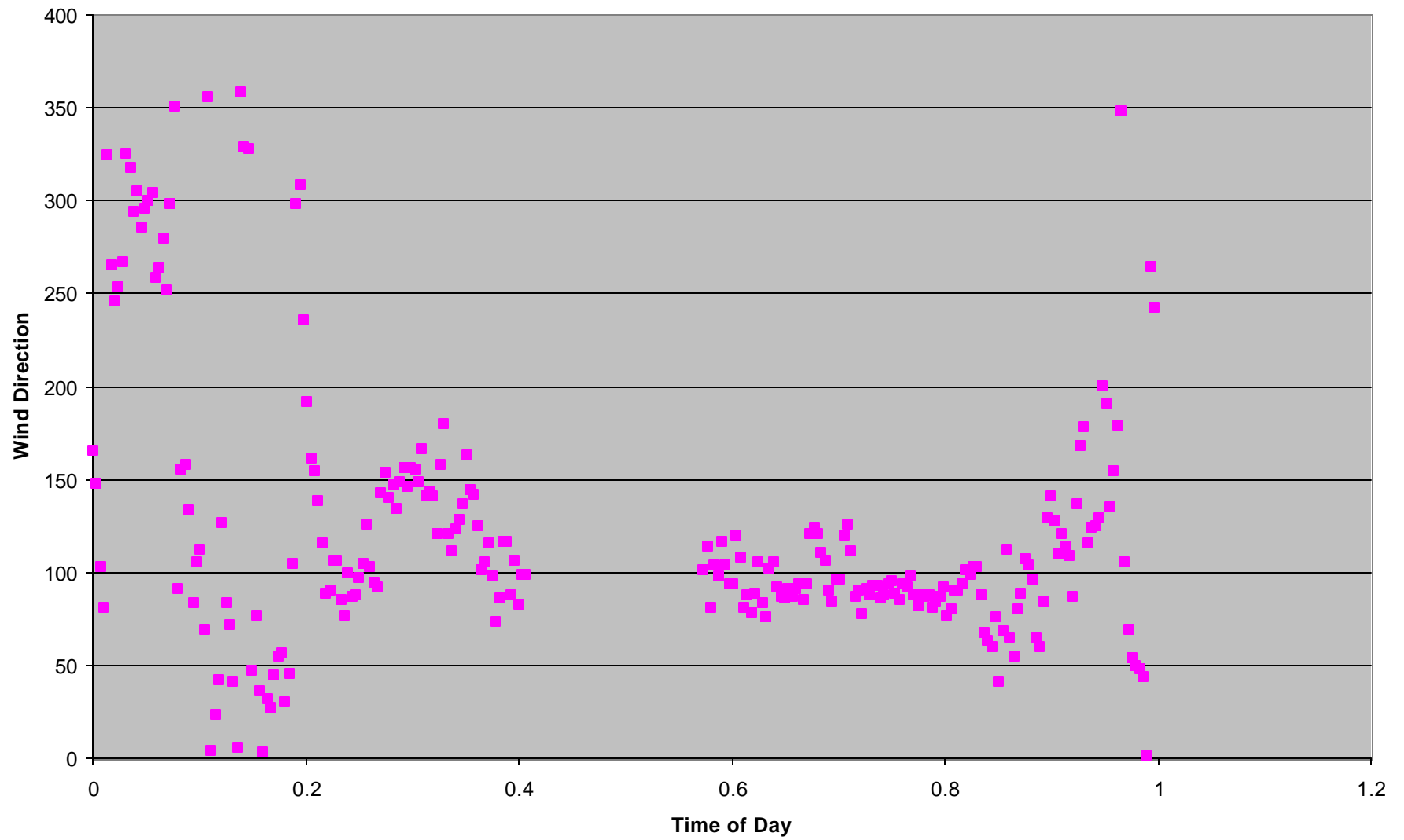
Contour Graph For Ambient Particle Mass Distribution
at Riverside at 03/01/01



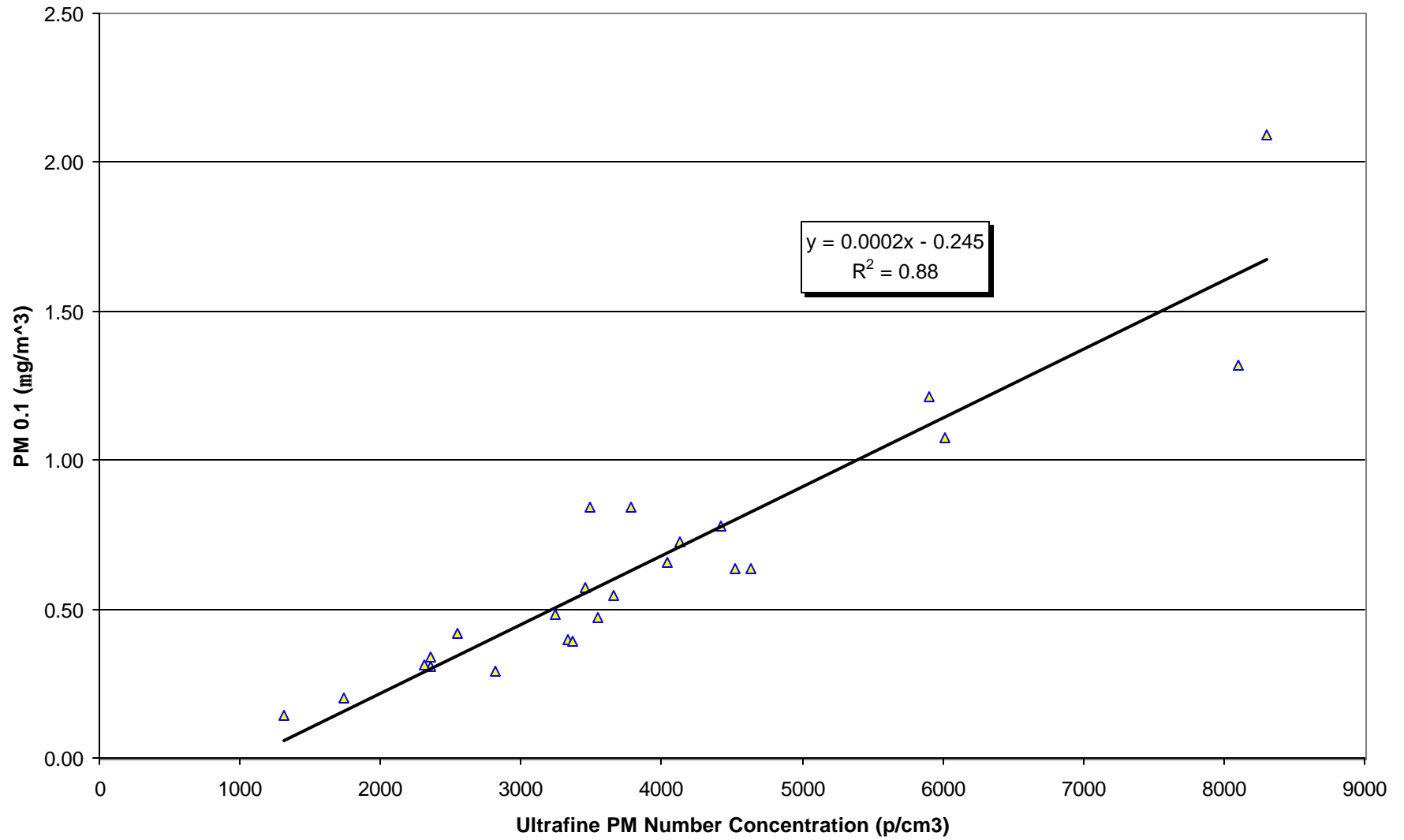
Wind Speed vs Time of Day. Riverside CA



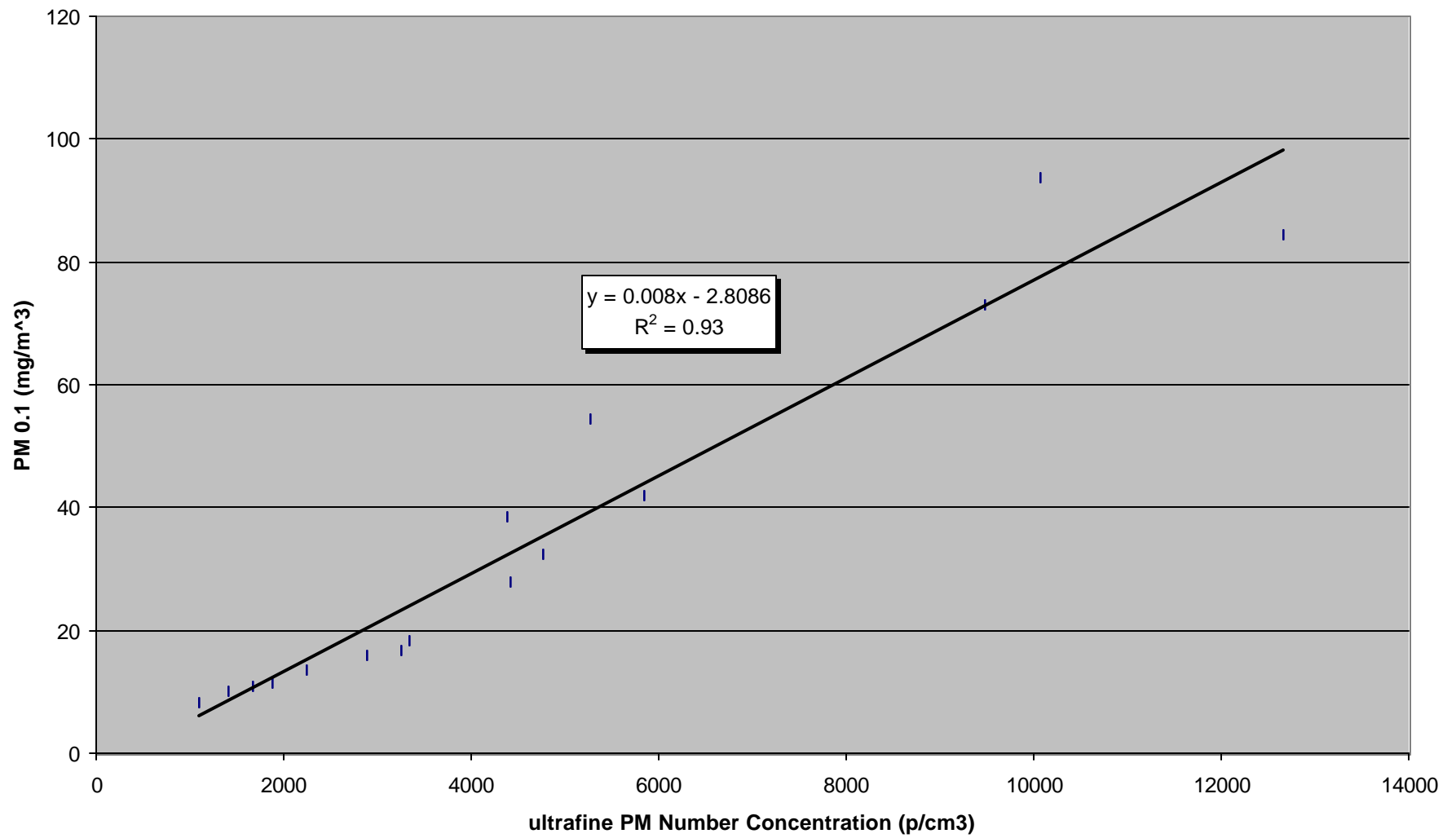
Wind Direction vs Time of Day. Riverside CA



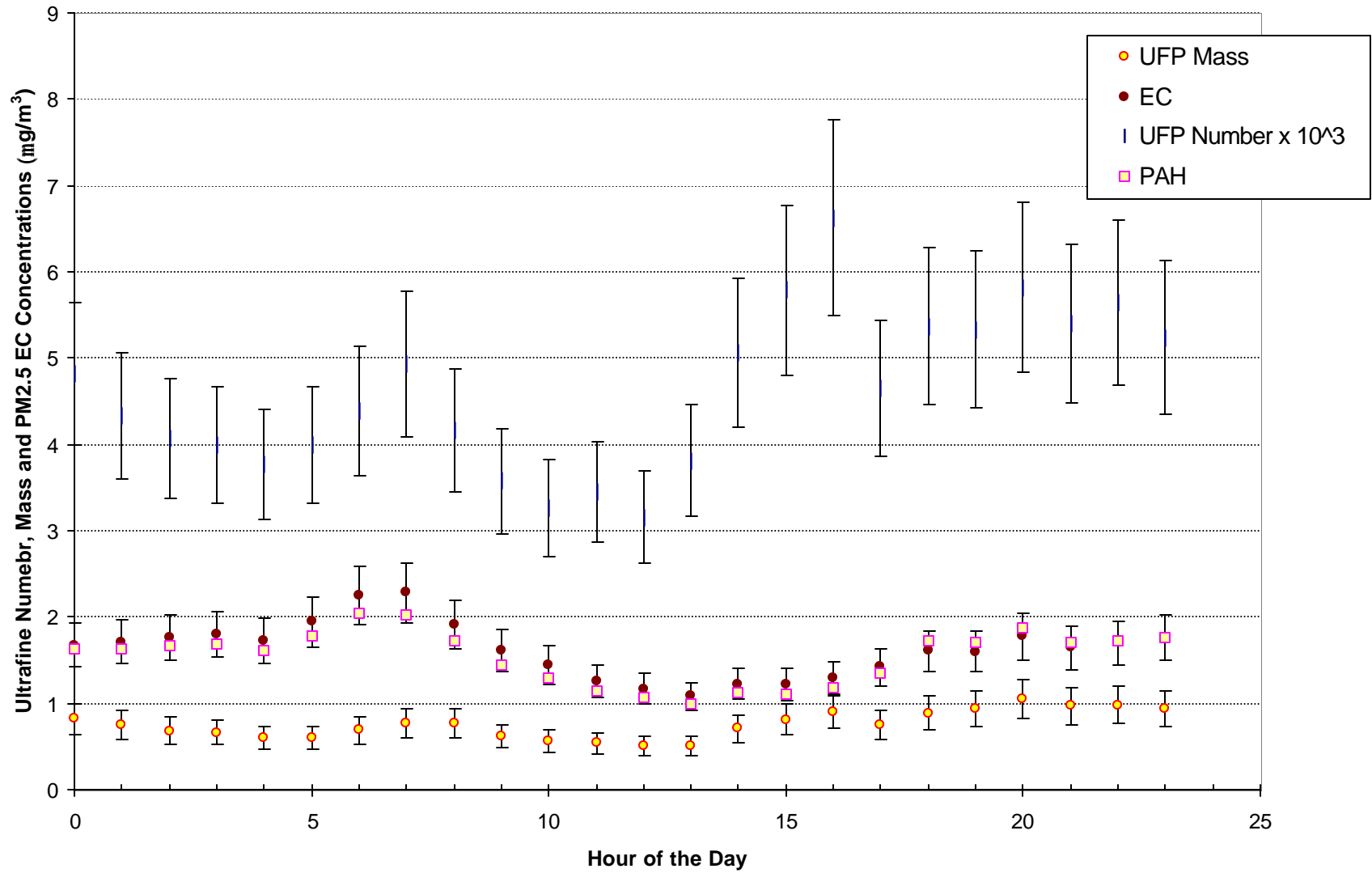
Ultrafine PM Mass vs Number Concentration
2/23/01



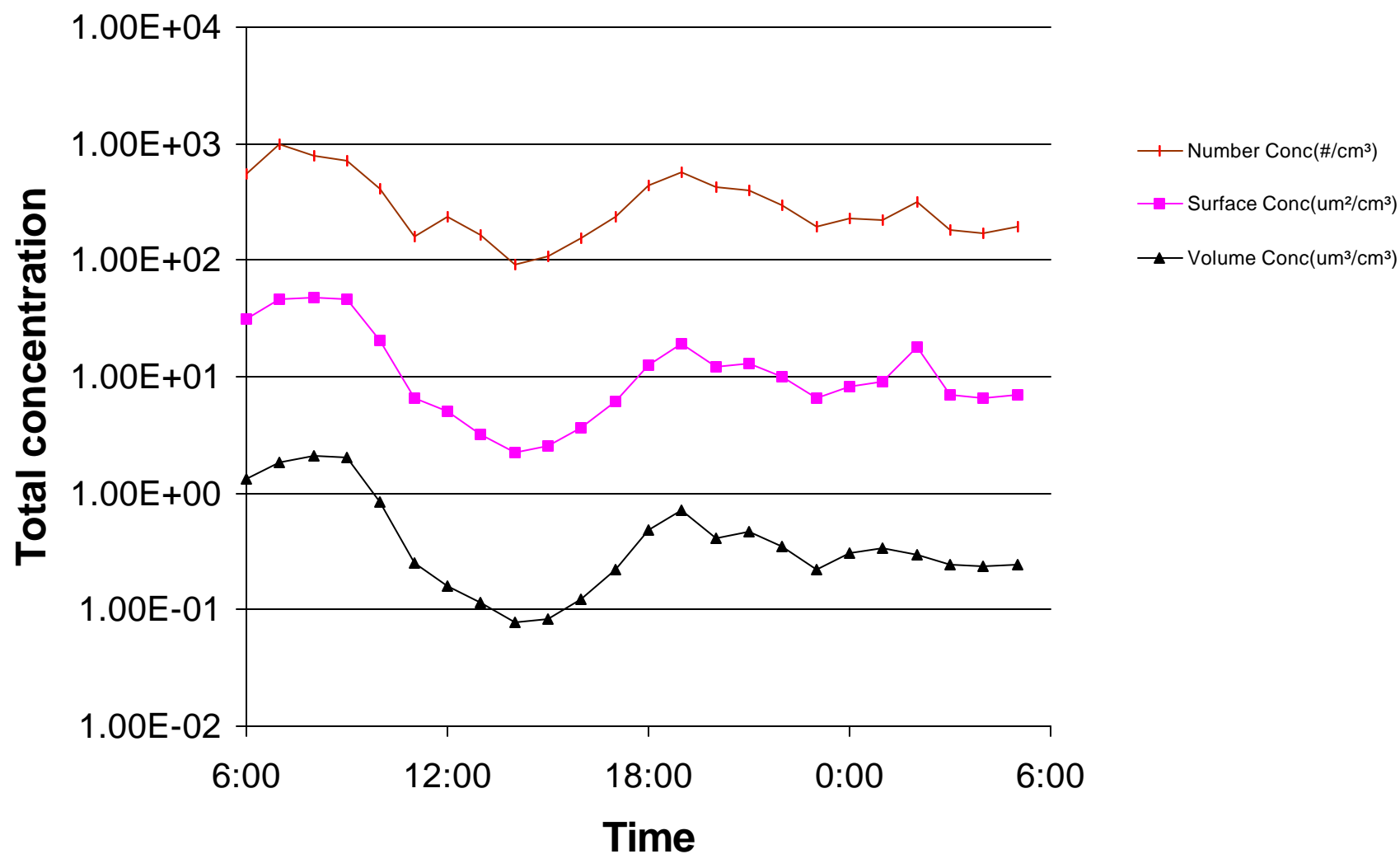
Ultrafine Number vs Mass concentrations
March 5, 2001



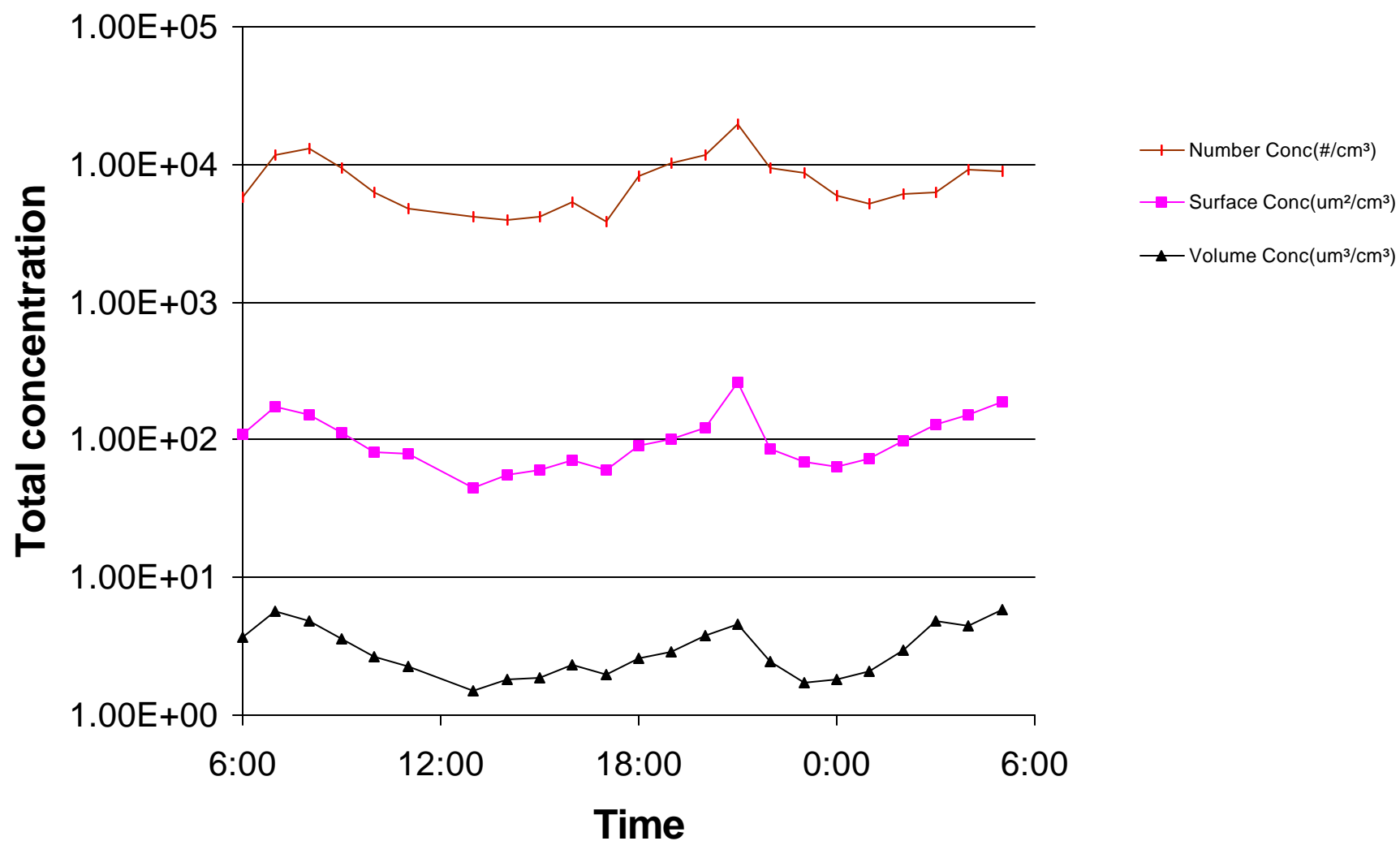
EC and Ultrafine PM Trends vs time of day

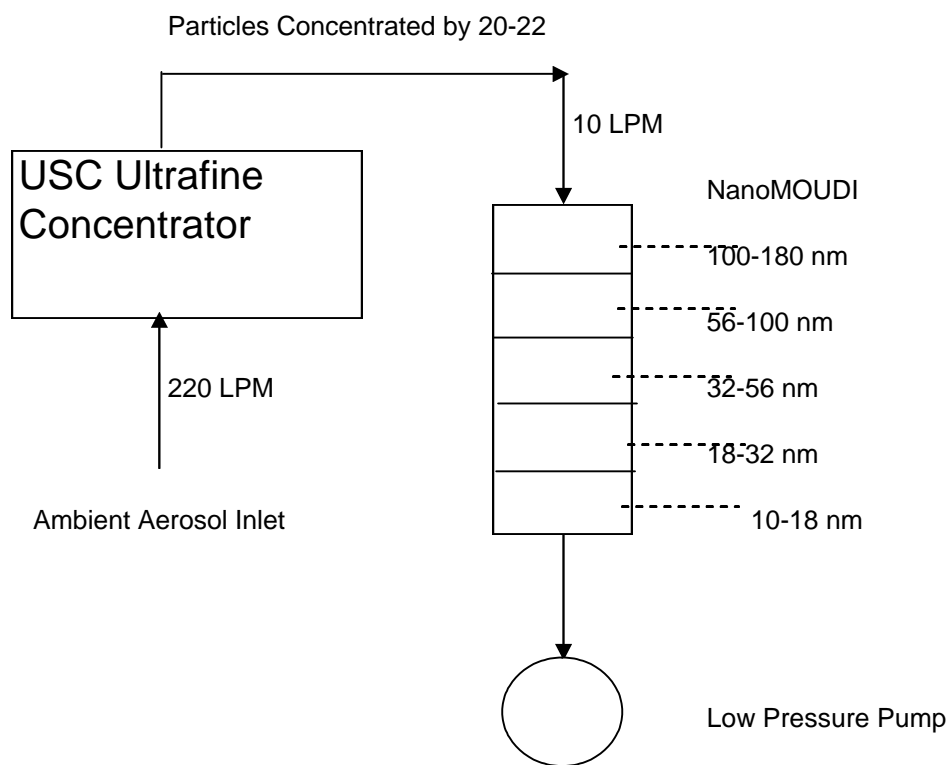


Total concentration of ambient particles at Rancho Los Amigos on 12/10/2000



Total concentration of ambient particles at Rancho Los Amigos on 10/10/2000





**Laboratory Characterization of the Ultrafine Concentrator Using
Indoor Aerosols as well as Ammonium Sulfate and Ammonium
Nitrate Aerosols**

